Study of the Chemistry of Soured and Chemically Treated Reservoir Fluids and Potential Impact on Microbial Influenced Corrosion in Oil and Gas Production Facilities

by

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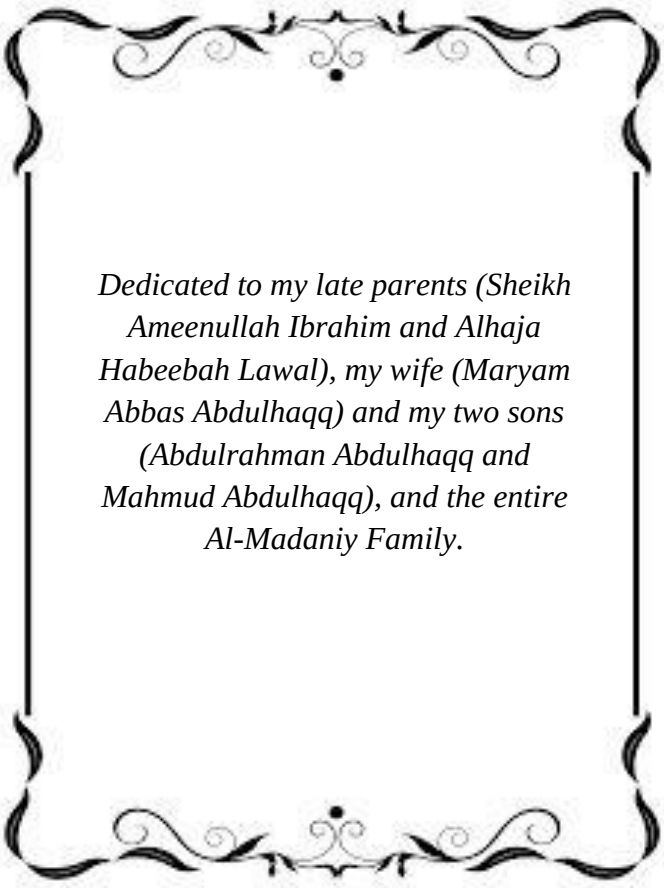
Dedicated to my late parents (Sheikh Ameenullah Ibrahim and Alhaja Habeebah Lawal), my wife (Maryam Abbas Abdulhaqq) and my two sons (Abdulrahman Abdulhaqq and Mahmud Abdulhaqq), and the entire Al-Madaniy Family.

ABSTRACT

The chemical environment (e.g. soured produced water, oil, limited oxygen environments) plays an important role in microbial activities leading to microbiologically influenced corrosion (MIC). The major cause of reservoir souring and subsequent corrosion in oil and gas facilities is the increased concentration of H_2S in the system. Among the microbial groups associated with MIC, sulfate-reducing bacteria (SRB) produce H_2S as a metabolic product of sulfate reduction in anaerobic respiration to obtain energy. To mitigate the SRB activities, nitrate or nitrite is injected in the reservoir to displace SRB with nitrate reducers. H_2S and other sulfur (S) species, and nitrogen (N) species (nitrate/nitrite) present can impact the chemistry of the system and microbial activities leading to MIC. Also, the chemical–microbial interactions complicate the understanding of chemical species transformation and partitioning behavior in gas, water, and oil and the subsequent impact on corrosion. Hence, it is essential to assess the impact of the chemical environment on microbial activities with respect to the corrosion processes in the oil and gas facilities. Several studies by microbiologists and corrosion scientists focused on the understanding of MIC mechanisms independent of the surrounding chemical environment. However, little is known about the dynamic behavior of the chemical environment and the reactivity between S and N species under various conditions.

This thesis advances the understanding of MIC in light of the surrounding chemical environment by identifying and analyzing different chemical species and transformations associated with MIC, resulting from biotic and abiotic processes. Microbial activities are found to overlap with chemical/electrochemical processes leading to corrosion. The

chemical environment, environmental factors, and microbial processes were examined to further understand the interactions and contributory impact on MIC. This work also describes the behavior of chemical species in a sulfide-oxic-nitrite environment as a function of temperature, pressure, and concentrations using equilibrium, and kinetic model approaches. The equilibrium simulation predicted the formation of S^0, FeS, $FeO(OH)$, and Fe_2O_3 as the key products, the amount of which varied depending on the chemistry and operating conditions. The kinetic model of the sulfide-oxic reaction in seawater showed a similar trend with the laboratory experiment in PW. The wet-lab experiments were conducted to study the reactivity of sulfide with nitrite under a range of conditions and generate kinetic data. Experiments indicated that sulfide in produced water (PW), seawater, and water is oxidized by nitrite to yield polysulfide, S^0, and NH_4^+ under weakly acidic to weakly basic conditions. However, sulfide forms insoluble FeS in the presence of Fe^{2+} in PW, which removes the sulfide from the oxidative transformation pathway.

The outcomes of this research provide a better understanding of the chemical environment impacting MIC. The understanding and information of S and N chemistry presented herein will provide insight into the chemical–microbial interactions in oil and gas operations under different conditions and inform further studies towards the development of robust MIC models.

ACKNOWLEDGEMENT

All praises and adorations are due to the Almighty Allah and may His peace and blessings be upon the noble Prophet Muhammad (SAW). To my late parents, Sheikh Ameenullah Ibrahim and Alhaja Habeebah Lawal; I owe it all to you. May your gentle souls rest in eternal bliss and Al-jannatul Firdaus!

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NOMENCLATURE

A: total number of atomic masses

a: number of atoms/activity of component *i* (mol/kg)

C_i: concentration of species *i* (mol/lit)

ΔG_f°: standard change in Gibb's energy of formation (J/kg)

G^t: total Gibbs free energy of the system (J/kg)

g_i: Gibb's energy of species *i* (J/kg)

k: chemical reaction rate constant

n_i : number of moles of the i^{th} species

P: pressure (kPa)

P^o: atmospheric pressure (kPa)

R: universal gas constant (8.314 kJ/kmol.K)

r: chemical reaction rate (mol/lit.sec)

T: absolute temperature (K)

y_i: mole fraction of species *i* in the gas phase

Greek letters

λ: Lagrange multiplier

γ: activity coefficient

φ: fugacity coefficient

α: stoichiometric coefficient

Superscripts

j: number of species phase in the system

Subscripts

i: number of chemical species in the system

k: number of elements in the system

m: number of chemical reactions

1 INTRODUCTION

1.1 Overview

In Canada, the oil and gas industry accounts for over 7% of the national GDP [1,2]. The safe operation of this huge infrastructure is critical to the well-being of workers, the public, and the environment. Most of the major accidents that occur in the oil and gas industry including oil spills, fire, and explosions, are due to infrastructure failure. Such occurrences may result in injury and loss of life, environmental damage, economic implications, and public distrust of the industry. Corrosion is the leading cause of oil and gas infrastructure failure and is estimated to cost as much as $7 Billion/yr [3,4]. Microbiologically Influenced Corrosion (MIC) accounts for at least 20 percent of all corrosion cases [5], yet, is poorly understood under most oil and gas operation conditions despite the decades of research. This is due to the lack of an interdisciplinary approach and advanced techniques of MIC investigation that would allow integration of findings and better understanding. Also, the traditional growth-based approaches targeted only limited microbial groups and activities [3]. Therefore, a multi-disciplinary examination of MIC (such as microbiology, corrosion, and material science, genomics, chemistry, modeling, and risk and safety engineering, etc.) is essential for understanding and managing MIC in the oil and gas industry. This research work focuses on the chemistry and chemical modeling of processes that may impact microbial activities; identifies key microbial-chemical precursors to MIC, examines the abiotic transformations of important chemical species, and contributes toward the development of models to predict/mitigate MIC.

Biogenic H_2S is formed in the reservoir by sulfate-reducing microorganisms (SRB) and transported to the topside of the offshore platform. It poses serious health concerns through inadvertent leaks and can lead to corrosion of the topside oil and water processing facilities. H_2S can also be transformed into different sulfur species depending on the operating conditions (e.g., pH, temperature, pressure, and composition), which may impact the microbial activities and the surrounding chemical environment leading to corrosion. Consequently, the application of nitrate and/or nitrite is used to prevent SRB activity and reservoir souring. Besides, nitrogen species and organic molecules in the system can also impact the chemical and microbial environments and they all play a critical role in corrosion on topsides. These chemical-microbial interactions have not yet been well understood.

In this research work, an extensive literature review was conducted on the microorganisms associated with MIC (nutrients, environmental factors, and metabolic products) as well as the chemical environment in the oil and gas operations such as produced water (PW) systems, oil and gas separators, and flowlines. The chemical compounds (corrosion products) found in different corrosive environments as deposits and/or scales were also reviewed. Furthermore, the chemistry of the local environment can have growth, inhibitory, or synergistic effects on microbial activity and hence MIC. Reactive species that are being utilized or produced via microbial activities may also undergo chemical transformations. This may lead to competition between chemical and microbial reactions, and the formation of compounds that inhibit or accelerate corrosion. It is therefore important to examine the role of the chemical environment and analyze the microbial-chemical interactions in MIC

propagation. The bulk of the recent works focus only on selected microorganisms, and microbial activities causing MIC rather than the chemistry of the environment where MIC takes place [6].

PW (formation and injected water containing production chemicals) is a complex mixture of dissolved and particulate organic and inorganic chemicals. It is generated during the production of oil and gas from onshore and offshore wells. The physical and chemical properties of PW vary widely depending on the geologic age, depth, and geochemistry of the hydrocarbon- bearing formation, as well as the chemical composition of the oil and gas phases in the reservoir, and production chemicals added to the production [13]. The offshore PW samples that were used in this research work were obtained from two offshore floating, production, storage and offloading (FPSO) oil recovery vessels; designated Platform 1 and Platform 2 (See Appendix). Both of these platforms are located approximately 350 km off of the east coast of Newfoundland and Labrador, Canada, in the Jeanne d'Arc Basin.

The modeling approach employed in this research work is based on a thermodynamic analysis of the system. The formation, dissociation, and stability of all chemical species in the system are based on the principles of thermodynamics and no chemical reaction can proceed except it is thermodynamically feasible. Both chemical and microbially mediated reactions follow the most thermodynamically favored pathways. However, some reactions proceed very fast before the equilibrium state is attained, which are not captured by the thermodynamics of the system at equilibrium. As a result of this, kinetic modeling is

essential for the reactions with available relevant data. This will give a better prediction of the chemistry of the system under different conditions with respect to time.

The study involves equilibrium and kinetic modeling of the chemical environment. A soured PW system subject to nitrate/nitrite treatment with the possibility of oxygen ingress was examined. The simulation was designed to study and analyze the potential influence of the sulfur (S) and nitrogen (N) species transformations on the overall chemistry of the system, which in turn, influences the microbial activities and/or electrochemical processes at the metal–environment interface. The computer modeling was followed by a well-designed wet-lab experiment with field PW samples, seawater, and water to investigate the reactivity of key S and N species, conduct kinetic studies of some important reactions, and validate the computer simulations.

1.2 Motivation and Scope

Corrosion is a major concern in the oil and gas industry. Owing to the high number of corrosion cases attributed to MIC in the industry, MIC has become a very important topic of research in recent years. A study in [14] reported that MIC has caused flow lines in Western Australia which were designed for more than 20 years to deteriorate in 3 years. The failure of the transit line which led to the largest Prudhoe Bay's oil spill in 2006 was attributed to MIC [15]. MIC can be caused due to the presence and/or activities of various microorganisms through different mechanisms. Such mechanisms may be complex due to the synergistic coexistence of different microorganisms and overlapping interactions between microorganisms and the chemical environment. However, regardless of the

pathway in which MIC is propagated, microorganisms require a medium with essential nutrients (organic and inorganic chemical species) and favorable conditions (temperature, pressure, pH, and concentration) to survive and thrive in the system. PW systems in the oil and gas topside facilities provide the source and sink of nutrients and favorable conditions for microbial activities. These lead to strong interactions between microorganisms and the chemical environment. Little is known about the behavior of the chemical environment and the chemical-microbial interactions in such systems. The dynamic responses of microbial activities due to changing process operating conditions, fluid composition, the complex relationship between the chemical and microbial processes account for the limited understanding.

Furthermore, chemical species in the system may undergo biogenic and/or non-biogenic transformations under different operating conditions. Such transformations have been studied for specific chemical species and conditions in the past. There are only a few studies on the chemical reactivity of these species under the PW system conditions and the corresponding impact on microbial activities leading to MIC. Therefore, a better understanding of these phenomena is important to fully describe the chemistry of the system. The research gaps identified are as follow:

- ✓ Limited understanding of microbial activities causing MIC, and connection to the chemical environments (chemical-microbial interactions).
- ✓ The need for identifying the important chemical species participating in MIC processes.

- ✓ The behavior of the chemical species transformations under different operating conditions and potential impact on MIC.
- ✓ Limited reactivity data of key chemical reactions involving S and N species in the produced fluid system.

The scope of this research covers the investigation and analysis of the fluid chemistry impacting MIC and determination of S and N species composition (as a function of temperature, pressure, composition, and pH) through chemical modeling and wet lab experiment. This study will contribute towards the development of the overall models to predict/mitigate MIC.

1.3 Objectives and Limitation

This research aims at investigating the chemical environment concerning the impact on microbial activities to better understand the chemical-microbial interaction in the oil and gas PW systems. The following are the research questions posed to achieve the set goal:

- ➢ What are the key players in MIC propagation and how these factors interact to propagate or inhibit MIC?
- ➢ What are the important chemical species that may impact MIC directly or indirectly in the chemical environment in which it occurs? Are there missing data?
- ➢ What is the transformation behavior of S and N chemical species in PW systems as a function of temperature, pressure, pH, and compositions?
- ➢ What is the reactivity of the S and N chemical species impacting MIC?

These research questions were answered, and the research gaps were filled through the following research objectives:

- ✓ To conduct an extensive review of general corrosion (precursors and products), fluid chemistry (seawater and PW), and microbial activities causing MIC (nutrients and metabolic products).
- ✓ To identify important chemical species in the oil and gas PW system which are precursors to MIC and collect relevant thermodynamic and kinetic data.
- ✓ To conduct detailed equilibrium modeling of the sour-oxic-nitrite environment as a function of pH, temperature, pressure, and composition and subsequently kinetic model with available reaction data.
- ✓ To study the reactivity of key chemical reactions involving S and N species and validate the model simulation with a wet-lab experiment using field PW samples.

Figure 1.1 shows the research tasks conducted and how they integrate to answer the research questions. The first task of this research work was the review and analysis of MIC and the surrounding chemistry. This task formed the basis for the entire research by providing insight and understanding of the interaction between microbial activities causing MIC and the chemical environment. Various important chemical species impacting MIC and information gaps were identified. The understanding and the information of the chemical species from task 1 were the inputs to the chemical environment modeling (second task). This task answered the research question related to the behavior of chemical species and transformation under different conditions. The third research task was the wet-

lab experiment, which was informed by the review and analysis of MIC and the chemical environment modeling. The task investigated the chemical reaction involving the important S and N species with limited understanding and information gaps. The outcomes of all the research tasks will inform further studies in this area and give insight into new research opportunities.

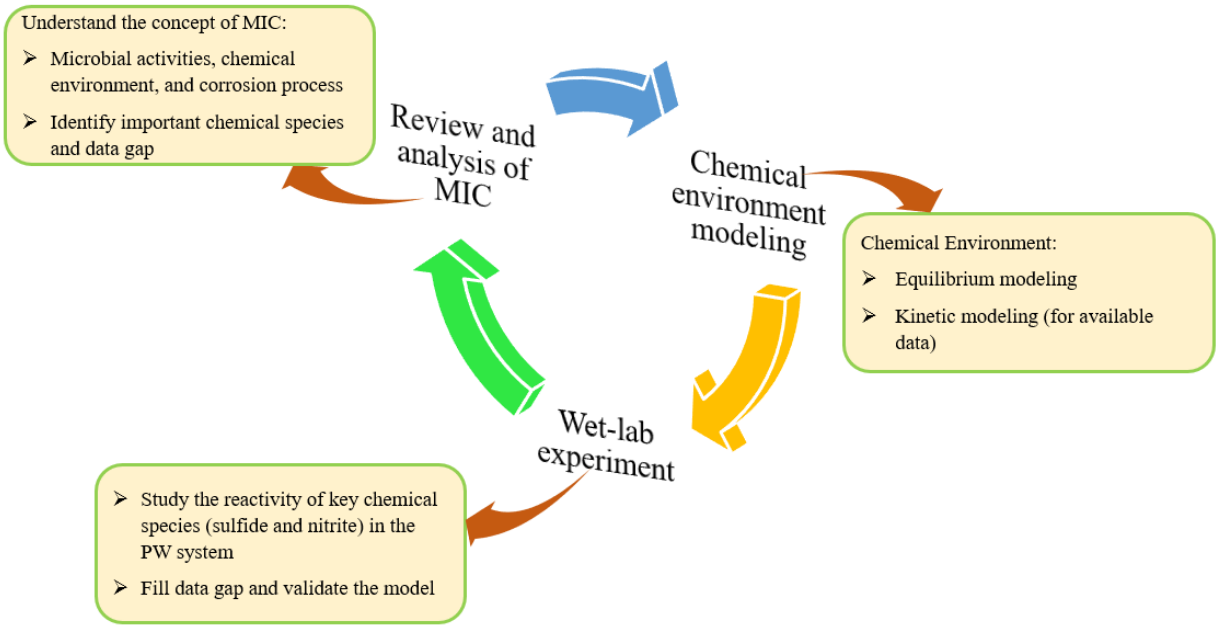

Figure 1.1: Research tasks of the thesis

The research activities of this thesis are limited to the investigation of the chemical environment and abiotic transformations of species to better understand the microbial-chemical interaction leading to MIC. Microbially-mediated transformations were not considered in the modeling or experimental work. In addition, the sulfide-oxic-nitrite environment was taken as a case study for this thesis. The wet lab experiments were conducted at atmospheric pressure and temperature not exceeding 60ºC, to ensure the operation was within the safety limit of the laboratory condition.

1.4 Contribution and Novelty

This section highlights the contributions and significance of this research work in the field of MIC and the chemical environment. A detailed description of each contribution is provided in the following sections:

1.4.1 Analysis of MIC with respect to the chemical environment

Many research works studying MIC focused on targeted microorganisms, and microbial activities causing MIC in isolation of the surrounding environment chemistry where MIC occurs. The chemical environment is an important factor to be considered in MIC propagation. It is the source and sink of microbial nutrients and by-products respectively and provides a suitable medium for the transformation of chemical species impacting microbial activities. Chapter 2 of this thesis presents a detailed review and analysis of MIC in the light of the surrounding fluid chemistry. This approach systematically examined various contributors to MIC propagation. These include microbial groups and activities causing MIC (e.g. nutrients, Physico-chemical parameters, metabolites), the chemical environment, and corrosion processes (precursors and products). The section presents pertinent information regarding the MIC chemistry in the oil and gas facilities including a comprehensive list of important chemical species. Critical arguments and illustrations were presented about the microbial-chemical interactions in MIC processes.

1.4.2 Equilibrium and kinetic modeling

Microbially mediated reactions associated with MIC have been studied extensively [7–11], without considering the relative impact of the chemically driven transformations of reactive species due to the changing operating parameters. Chapter 3 of this thesis demonstrates the dynamic behavior of the chemical environment as a function of temperature, pressure, and composition to represent the offshore oil and gas topside conditions. Equilibrium and kinetic models were used to simulate the chemistry of fluids with the goal to understand the behavior of various chemical species and impact on MIC in a given environment. The sour-oxic-nitrite environment was considered in this current work. The outcomes of this study were information to the microbiological studies and simulations to predict chemical species composition as a function of operating parameters, which can be incorporated in the overall MIC mechanism and risk models.

1.4.3 Experimental investigation of sulfide–nitrite chemical transformation

Little is known about the reactivity between S and N species in the PW system and potential impacts on corrosion. It is a common belief among researchers that sulfide can react chemically with nitrite [11,12] in the PW system, however, there are no kinetic studies conducted on the sulfide-nitrite chemical reaction in produced fluids targeting the offshore oil and gas applications. Chapter 4 presents a reactivity study of sulfide and nitrite in different media including PW, seawater, and water. Experiments suggested that sulfide in these media could be oxidized by nitrite to polysulfide, elemental sulfur, and ammonium under weakly acidic to weakly basic conditions, and kinetic data were generated under the

experimental conditions. The outcome of this study provides a better understanding of the chemistry of sulfide and nitrite transformation in PW, seawater, and water systems, and reaction data which will inform further studies.

1.5 Organization of the Thesis

This thesis is written in a manuscript-based format. The outcomes of this thesis are three submitted peer-reviewed journal papers. Figure 1.2 shows the organizational structure of this thesis. Chapters 1 and 5 are the introduction and conclusions, respectively. Chapters 2 to 4 of this thesis are developed based on the paper submissions to peer-reviewed journals.

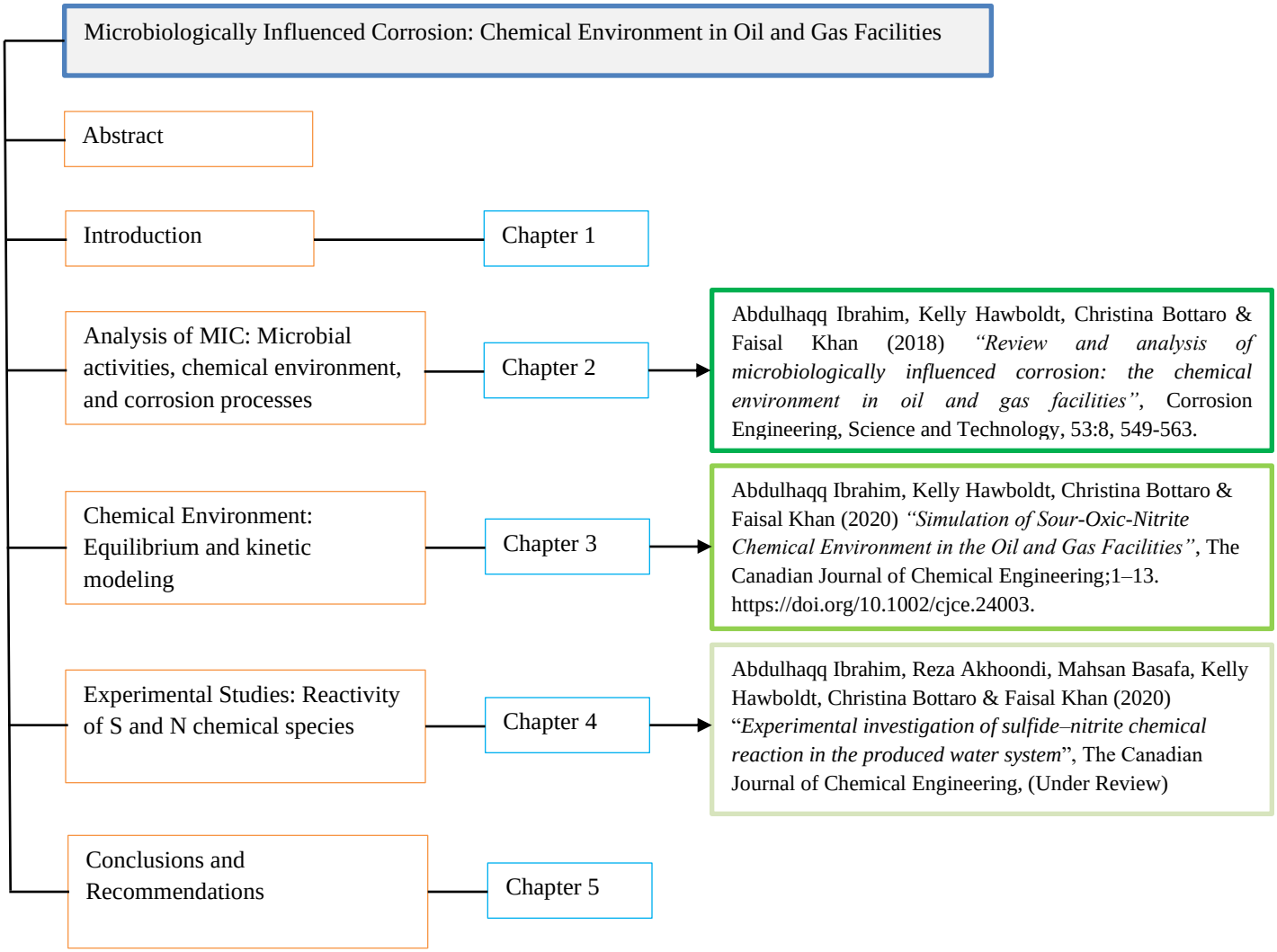

Figure 1.2: Structure of the Ph.D. thesis and related publications

1.6 Statement of Co-Authorship for Journal Articles

I have worked with a team of researchers of various expertise to complete the agreed research tasks. The outcomes of these research tasks were published in peer-reviewed journals with co-authors who have directly contributed to the work. Below are the details of the contributions.

Paper 1 (Chapter 2): Abdulhaqq Ibrahim, Kelly Hawboldt, Christina Bottaro & Faisal Khan (2018) "Review and analysis of microbiologically influenced corrosion: the chemical environment in oil and gas facilities", Corrosion Engineering, Science and Technology, 53:8, 549-563, DOI: https://doi.org/10.1080/1478422X.2018.1511326

Abdulhaqq Ibrahim: Lead author, developed the research problem, conducted the review and analytical study, and wrote the first draft of the manuscript and subsequent revisions. Kelly Hawboldt: assisted in developing the research problem and analysis of information; reviewed the draft and made revisions. Christina Bottaro: reviewed and edited the manuscript. Faisal Khan: helped to review and revise the draft.

Paper 2 (Chapter 3): Abdulhaqq Ibrahim, Kelly Hawboldt, Christina Bottaro & Faisal Khan (2020) "Simulation of Sour-Oxic-Nitrite Chemical Environment in the Oil and Gas Facilities", The Canadian Journal of Chemical Engineering;1–13, DOI: https://doi.org/10.1002/cjce.24003

Abdulhaqq Ibrahim: Lead author, developed the research problem, collected data, and conducted modeling study, and wrote the first draft of the manuscript and subsequent revisions. Kelly Hawboldt: assisted in the model development and analysis of results; reviewed the draft and made revisions. Christina Bottaro: helped in the result analysis, reviewed, and edited the manuscript. Faisal Khan: helped to review and revise the draft.

Paper 3 (Chapter 4): Abdulhaqq Ibrahim, Reza Akhoondi, Mahsan Basafa, Kelly Hawboldt, Christina Bottaro & Faisal Khan (2020) "Experimental investigation of

sulfide–nitrite chemical reaction in produced water system", The Canadian Journal of Chemical Engineering, (Under review)

Abdulhaqq Ibrahim: Lead author, developed the research plan and experimental design and setup, conducted experiments and analyzed results, and wrote the first draft of the manuscript and subsequent revisions. Reza Akhoondi: helped to set up experiments, analyzed experimental samples and interpreted the results. Mahsan Basafa: helped in the analysis and interpretation of results and reviewed the manuscript. Kelly Hawboldt: assisted in the experimental design and analysis of results; reviewed the draft and made revisions. Christina Bottaro: helped in the result analysis, reviewed, and edited the manuscript. Faisal Khan: helped to review and revise the draft.

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2 REVIEW AND ANALYSIS OF MIC: THE CHEMICAL ENVIRONMENT IN OIL AND GAS FACILITIES

Preface

A version of this manuscript has been published in the Journal of Corrosion Engineering, Science and Technology (https://doi.org/10.1080/1478422X.2018.1511326). I am the primary author of this work. Along with me are the co-authors; Kelly Hawboldt, Christina Bottaro and Faisal Khan. I conceptualized the idea and conducted the literature review. I carried out the data collection, analysis, and visualization. I prepared the original draft of the manuscript and subsequently revised the manuscript based on the co-authors' feedback. The co-author Kelly Hawboldt supervised the work, helped in the concept development, reviewed, and edited the manuscript. The co-authors Christina Bottaro and Faisal Khan contributed in preparing, reviewing, and editing the manuscript. The co-authors helped in identifying the information gaps highlighted in the work.

Publication:

Abdulhaqq Ibrahim, Kelly Hawboldt, Christina Bottaro & Faisal Khan (2018) *"Review and analysis of microbiologically influenced corrosion: the chemical environment in oil and gas facilities"*, Corrosion Engineering, Science and Technology, 53:8, 549-563, DOI: https://doi.org/10.1080/1478422X.2018.1511326

Abstract

Microbiologically influenced corrosion (MIC) is a complex phenomenon requiring integrated knowledge of multiple disciplines to better manage and mitigate impacts. The chemical environment (e.g. produced water, soured oil) plays an important role in MIC. Chemical reactions and phase changes due to temperature, pressure, pH and to a lesser extent salinity, impact microbial activities which in turn influences the surrounding chemical environment leading to corrosion. The chemical–microbial interactions complicate the understanding of chemical species transformation and partitioning behavior in gas, water and oil and subsequent impact on corrosion. In this paper, a review of the complex chemical transformations of chemical species resulting from biotic and abiotic processes are presented. These chemical species can have growth, inhibitory or synergistic effects on microbial activities causing MIC. Microbial activities are found to overlap with chemical/electrochemical processes leading to corrosion. The interaction between chemical environment, environmental factors, electrochemical and microbial processes has been explained with examples from the literature, to understand the contributory effects on MIC. This study will inform further investigation on the chemical environment impacting MIC and model development.

Keywords: Microbiologically Influenced Corrosion (MIC), microbial activities, chemical environment, chemical species, and environmental factors.

2.1 Introduction

Microbiologically influenced corrosion (MIC) is the microbial modification of the chemical environment at the metal interface, causing accelerated corrosion of metals [1,2]. Rapid corrosion of iron metal and steel has been attributed to microbial processes present in soil, freshwater, seawater, crude oil and its derivatives, process chemicals and sewage [3]. MIC is a concern in many industrial processes such as oil and gas production, storage and pipeline transportation, power generation, as well as water and waste-water systems. Microbial activities contribute to reservoir souring, equipment and pipeline deterioration due to corrosion [4], and consequently cause pipeline rupture. Oil and Gas pipeline failures due to MIC could lead to oil spillage.

MIC has been reported to cause 20% cost of the total damage due to corrosion [5]. About 10% of corrosion cases in the UK has been attributed to microbial activities [6]. A study in [7] reported that MIC has caused flow lines in Western Australia which were designed for more than 20 years to deteriorate in 3 years. The failure of the transit line which led to the largest Prudhoe Bay's oil spill in 2006 was attributed to microbial corrosion [8]. Despite various attempts in the past years to describe MIC-related infrastructural failures, the relationship between microbial activities and the corrosion, and chemical environment is not fully understood. MIC has been studied by various disciplines in isolation and independent of one another. Perhaps, this might have limited the advances in the understanding of MIC. Therefore, it is important to identify the interconnection between

the microbial activity, corrosion process and chemistry of the environment (Figure 2.1), for better understanding of MIC.

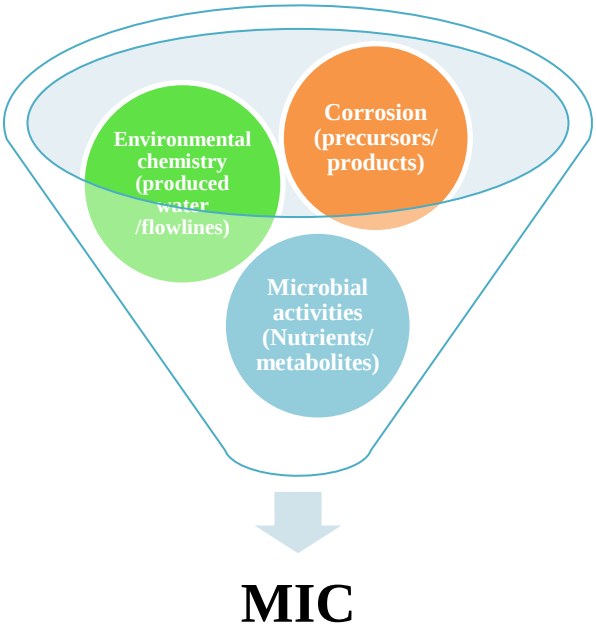

Figure 2.1: Interactions between microbes, corrosion, and environment

This paper focuses on reviewing the groups of microbes associated with MIC (nutrients, physico-chemical conditions, and metabolic products) as well as the chemical environment in the oil and gas operations such as produced water systems, separators, and flowlines. The chemical compounds (corrosion products) found in different corrosive environments were also reviewed. The chemistry of the local environment can have growth, inhibitory, or synergistic effects on microbial activity and hence MIC. Reactive species that are being utilized or produced via microbial activities may as well undergo chemical transformations under certain thermophysical conditions. This may lead to co-utilization/production and/or counter-utilization/production of chemical species in the environment. It has been noticed

that the bulk of the recent works focus on the microbes, and microbial activities causing MIC rather than the chemistry of the environment where MIC takes place. The sections included in this paper present pertinent information followed by critical argument in relation to microbial activities/MIC and chemical environment. Figure 2.2 outlines the structure and organization of the paper.

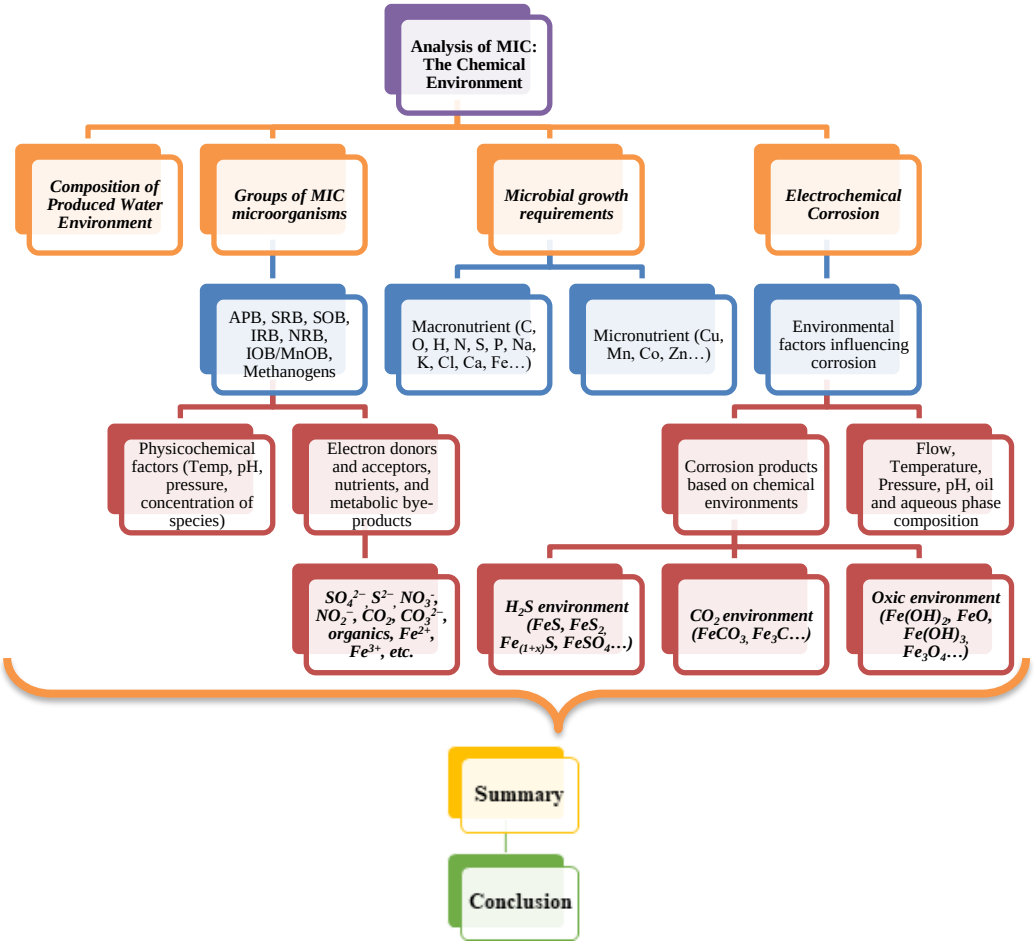

Figure 2.2: Organizational chart of the paper

2.2 MIC and Microbial Growth Requirements

Microbiologically influenced corrosion (MIC) can be defined as the corrosion due to the presence and/or activities of microbes such as bacteria, microalgae, and fungi. According to [9], MIC refers to the influence of microorganisms on the kinetics of corrosion processes of metals, caused by microorganisms within the biofilm adhering to the interfaces. Microbial activities do not give rise to a unique type of corrosion. However, influence and/or accelerate the rates of partial reactions at the anode or cathode in corrosion processes, thereby shifting the corrosion mechanisms [3,10]. For example, the metabolic activity of biofilm microbes can alter the local physico-chemical conditions (O_2 concentration, pH level, redox potential and conductivity) at the interface [9]. Such conditions can displace the corrosion potential towards a more positive potential and subsequent increased susceptibility of metal surface to localized corrosion including pitting, hydrogen embrittlement, and stress corrosion cracking [3,11]. The activities of microorganisms could also lead to reduction of metal oxide, production of acid or localization of anodic site at the metal interface [12].

MIC can be initiated and propagated via the biofilm by physical deposition, production of corrosive by-products (metabolites), and depolarization of corrosion cell due to chemical reactions [13]. The formation of biofilms on metal surface may result in conditions such as pH, concentration of ions, and O_2 levels at the micro-environment within the biofilm to be different from the surrounding environment, enhancing ennoblement [14]. Ennoblement is an increase in corrosion potential (E_{corr}) caused by the microbial activity within biofilms.

The probability of localized corrosion increases as the E_{corr} approaches the pitting potential (E_{pit}) [15]. Ennoblement increases the rate of cathodic reactions on the metal, and hence, influences corrosion [11,12]. Microorganisms may produce acidic metabolites such as organic acids, and hydrogen sulfide (H_2S) within the biofilm. These corrosive by-products can concentrate at the metal surface, leading to an accelerated localized attack. Depolarization is the removal of reaction product from an electrode site. The microbial consumption of hydrogen gas (H_2) surrounding the cathode, produced electrochemically by reduction of protons with electrons derived from iron oxidation, can also stimulate further corrosion [13]. As such, conditions that enhance or inhibit microbial growth are important.

The metabolism of microorganisms is dependent on the availability of an energy source, carbon source, nutrients, electron donors and acceptors, and water [16]. A summary of requirements for microbial growth are presented in Table 2.1.

Table 2.1: Prerequisite for the growth of microorganisms [9].

Prerequisite	Source	Growth type
Carbon source	Carbon dioxide (CO_2), Organic substances/Hydrocarbons	Autotrophic, Heterotrophic
Energy source	Light, Chemical substances	Phototrophic, Chemotrophic
Electron donor (oxidized)	Inorganic substances, Organic substances	Lithotrophic, Organotrophic
Electron acceptor (reduced)	O_2, NO_2^-, NO_3^-, SO_4^{2-}, CO_2	Aerobic, anoxic, anaerobic

Nutrients required by microorganisms are categorized into those needed in large quantities (macronutrient) and those which are required only in trace amounts (micronutrient). There are six major elements among the macronutrients which constitute the necessary biological macromolecules including C, O, H, N, S, and P. Other macronutrients such as Ca, Mg, Na, K, and Fe exist as ions and are required in lesser amount for a range of functions [17]. Table 2.2 summarizes the form of supply and functions of the macro and micro elements found in living organism.

Table 2.2: Mineral nutrients requirement of microorganism [17].

Element	Form in which usually supplied	Occurrence/Function in biological systems
Macronutrients		
Carbon (C)	CO_2, organic compounds	Component of all organic molecules, CO_2
Hydrogen (H)	H_2O, organic compounds	Component of biological molecules, H+ released by acids
Oxygen (O)	O_2, H_2O, organic compounds	Component of biological molecules; required for aerobic metabolism
Nitrogen (N)	NH_3, NO_3^-, N_2, organic N compounds	Component of proteins, nucleic acids
Sulfur (S)	H_2S, SO_4^{2-}, organic S compounds	Component of proteins; energy source for some bacteria
Phosphorus (P)	PO_4^{3-}	Found in nucleic acids, ATP, phospholipids
Potassium (K)	In solution as K^+	Important intracellular ion
Sodium (Na)	In solution as Na^+	Important intracellular ion
Chlorine (Cl)	In solution as Cl^-	Important intracellular ion
Calcium (Ca)	In solution as Ca^{2+}	Regulator of cellular processes
Magnesium (Mg)	In solution as Mg^{2+}	Coenzyme for many enzymes

Iron (Fe)	In solution as Fe^{2+} or Fe^{3+} or as FeS, $Fe(OH)_3$ etc.	Carries oxygen; energy source for some bacteria
Micronutrients	Present as contaminants at very low concentrations	
Copper (Cu)	In solution as Cu^{+}, Cu^{2+}	Coenzyme; microbial growth inhibitor
Manganese (Mn)	In solution as Mn^{2+}	Coenzyme
Cobalt (Co)	In solution as Co^{2+}	Vitamin B_{12}
Zinc (Zn)	In solution as Zn^{2+}	Coenzyme; microbial growth inhibitor
Molybdenum (Mo)	In solution as Mo^{2+}	Coenzyme
Nickel (Ni)	In solution as Ni^{2+}	Coenzyme

Microorganisms derive carbon from CO_2 or organic sources (chemical compound with C–H bond) and often fulfill their nutrient requirement from the oxyanions of some base elements, e.g. PO_4^{-3}, SO_4^{-2}, NO_3^{-}, NO_2^{-} [12]. Nutrients such as SO_4^{-2}, NO_3^{-} and PO_4^{-3} alter the minimum critical potential (ratio of corrosive ions to inhibiting ions) [18,19]. Conditions where the critical potential is below the minimum critical potential do not favour localized corrosion. Oxyanions such as SO_4^{-2}, NO_3^{-}, NO_2^{-}, PO_4^{-3}, CIO^{-4} and OH^{-} can be reduced or assimilated by microbes, this will impact the chemistry of the system and corrosion [19].

Organic compounds including hydrocarbons such as alkanes and alkenes (C_1-C_{30}), and aromatic compounds (alkylbenzenes) are the main constituents of oil and gas. Organic compounds are substrates or carbon sources for aerobic and/or anaerobic microbes such as denitrifying, sulfate-reducing and ferric iron-reducing bacteria [20]. The availability of organic compounds/hydrocarbons coupled with sources of electron donors and acceptors

in the oil and gas facilities and flowlines may create favorable condition for microbial growth and therefore the infrastructures are highly prone to MIC.

2.3 Groups of MIC Microorganisms

Sulfate-reducing bacteria (SRB) has been identified as the leading cause of MIC in cast, mild iron, and stainless steel, where sulfate is present [21]. Other microorganisms associated with corrosion are acid-producing bacteria (APB), nitrate-reducing bacteria (NRB), sulfur-oxidizing bacteria (SOB), iron oxidizing/reducing-bacteria (IOB/IRB) and manganese-oxidizing bacteria (MnOB) [3,15]. These microorganisms often exist synergistically in colonies and enhance each other's growth [13]. The diversity and distribution of microbial species in a biofilm colony do not only depend on biotic factors. Abiotic conditions such as the chemical environment, nutrient levels, O_2 concentration, pH, and temperature may impact the microorganisms as well [22].

Acid-producing bacteria (APB) include heterotrophic bacteria that metabolize organic substrates to generate organic acids (eq. 1) such as formic acid (HCOOH), acetic acid (CH_3COOH), and lactic acid ($CH_3CHCOOH$). An acidic condition is developed at the biofilm-metal interface which may cause a shift in the local pH and provoke corrosion to occur [23]. *Clostridium aceticum* is an example of organic acid-producing bacteria and *Thiobacillus* are those that produce inorganic acids such as sulfuric acid [3]. Many APB can tolerate acidic environment such as *Thiobacillus* which can survive in a pH as low as 1 [9]. The facultative nature of APB allows them to survive under wide range of conditions, switching from aerobic to anaerobic respiration in the almost absence of O_2. The O_2

beneath the biofilm is depleted through the APB metabolism thereby creating an O_2 free environment which allows the anaerobic activities of sulfate-reducing bacteria (SRB) to take place[24].

$$(CH_2O)_n \xrightarrow{\text{fermenters}} (\text{organic acids, alcohols, } CO_2, H_2 \text{ and } H_2O) \quad \text{(Eq. 1)}$$

Sulfate-reducing bacteria (SRB) have been identified in the crude oil as the primary cause of MIC in pipelines. SRB are ubiquitous and diverse group of anaerobic microbes that derive energy from organic compounds of low molecular weight, such as hydrocarbons, alcohols, aromatic compounds and mono- or dicarboxylic aliphatic acids (lactate and acetate) or H_2 [25,26]. SRB utilize sulfate ion (SO_4^{-2}) as the terminal electron acceptor (eq. 2) to produce H_2S or HS^- as the product [3,27]. H_2S reacts aggressively with metallic iron to produce iron sulfide (eq. 3) [28].

$$SO_4^{2-} + 10H^+ + 8e^- \longrightarrow H_2S + 4H_2O \quad \text{(Eq. 2)}$$

$$H_2S + Fe^0 \longrightarrow FeS + H_2 \quad \text{(Eq. 3)}$$

Many SRB can also reduce nitrate (NO_3^-), elemental sulfur, sulfite (SO_3^{-2}) and thiosulfate ($S_2O_3^{-2}$) [3]. These microbes typically grow in a pH range between 4.0–9.5, a temperature range of 298.15–333.15 K and can tolerate up to 50.6 MPa pressure [3,29]. *Desulfovibrio* species are example of SRB found to be the very corrosive.

Sulfur-oxidizing bacteria (SOB) are mostly aerobic microbes which oxidize inorganic sulfur compounds such as metal sulfides, H_2S, SO_3^{-2}, $S_2O_3^{-2}$ and elemental sulfur to obtain the energy required for growth [3,30], (eq. 4–6). The metabolic by-products of these

microbes are sulfuric (H_2SO_4) and sulfurous acid (H_2SO_3) [13], which are very aggressive and corrosive to iron and steel. H_2SO_4 and HNO_3 react with metals to form products soluble salts, and therefore do not deposit on the metal surface, exposing the surface to further corrosion [9]. The type of SOB present depends on the carbon and energy sources. Some may thrive in CO_2 and inorganic environments while others derive energy and carbon from organic compounds [31]. One of the common genera of SOB are *Acidithiobacillus species* which mainly use O_2 for metabolism and obtain carbon from CO_2 with optimum temperature and pH of 293.15–323.15 K and <2-8 respectively [32].

$$2S + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4 \quad \text{(Eq. 4)}$$

$$H_2S + 2O_2 \longrightarrow H_2SO_4 \quad \text{(Eq. 5)}$$

$$12H_2S + 6S_2O_3^{2-} + 9O_2 \longrightarrow 12H_2SO_4 \quad \text{(Eq. 6)}$$

Iron reducing bacteria (IRB) is a group of facultative microorganisms which has been proposed in MIC [12]. These microbes can use O_2 aerobically and switch to anaerobic respiration in the absence of O_2 [33]. IRB derive benefit anaerobically by reducing insoluble ferric ions (Fe^{3+}) to soluble ferrous ions (Fe^{2+}), (eq. 7) while the reducible Fe^{3+} is utilized as the terminal electron acceptor during metabolism [34,35].

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad \text{(Eq. 7)}$$

The process of Fe^{3+} reduction facilitates the corrosion of iron and its alloys by removing the protective corrosion products formed or corrosion-resistant oxide films and exposes metal surfaces to further attack [9,36]. The iron reducers thrive well in neutral pH

environment, like most other bacteria especially the SRB and NRB. *Pseudomonas and Shewanella* genera are examples of bacteria capable of reducing iron and/or manganese oxide among others [9].

Nitrate-reducing bacteria (NRB) are facultative microorganisms known as denitrifying bacteria. These microbes utilize NO_3^- as an oxidizing agent and the terminal electron acceptor in the absence of molecular oxygen. *Pseudomonas* and *Achromobacter* genera are examples of NRB [9]. NO_3^- reduction (eq. 8) is a major metabolism of microbes under anoxic conditions [37].

$$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O \qquad \text{(Eq. 8)}$$

NO_3^- has been used to mitigate SRB activities and control MIC [38]. The addition of NO_3^- stimulates the activities of heterotrophic nitrate-reducing bacteria (NRB) and sulfide-oxidizing, nitrate-reducing bacteria (soNRB) to outcompete SRB for hydrocarbons. The production of nitrite and nitrous oxides inhibit the sulfate reducing activity, and sulfide production of SRB [39,40].

Iron/Manganese-oxidizing bacteria (IOB/MnOB) is an aerobic group of microorganisms known as metal-depositing bacteria. IOB oxidize soluble ferrous (Fe^{2+}) to ferric (Fe^{3+}) to derive energy, which may result in a dense deposit on the metal surface (eq. 9). Most IOB thrive at neutral pH with low O_2 concentration (microaerophilic) [41]. An example of the bacteria in this group is *Gallionella*. The oxides of the Fe and Mn ions deposited are reactive and promote cathodic reduction leading to corrosion [9].

$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-} \quad \text{(Eq. 9)}$$

Methanogens are microorganisms that utilize organic compounds, CO_2 or H_2 to produce methane (CH_4) as metabolites during anaerobic respiration (eq. 10) [37]. Methanogenic archaea have been identified as important contributors to MIC, leading to pitting corrosion of steel pipes in anoxic marine environments [42,43].

$$HCO_3^- + 9H^+ + 8e^- \longrightarrow CH_4 + 3H_2O \quad \text{(Eq. 10)}$$

Methanogens use Fe^0 oxidation for growth and energy generation through cathodic depolarization. The H_2 released is then consumed by the methanogens, leading to further oxidation of the iron metal in anaerobic environments [44]. *Methermicoccus* and *Methanobacterium* species are examples of corrosive methanogens [45].

Table 2.3 summarizes the nutritional requirements of different groups of microorganisms associated with MIC, and possible end products [46].

Table 2.3: Summary of nutritional requirements of various groups of MIC microorganisms and possible end products.

Group	Example of Species	pH	Temperature (K)	Nutrient	End product
Sulfate-reducing bacteria (Anaerobic)	*Desulfo-vibrio*	4 – 9.5	298.15 – 333.15	Organic compounds, hydrocarbons, alcohols, aromatic compounds lactate, and acetate or H_2. SO_4^{-2}, elemental sulfur, sulfide and thiosulfate ($S_2O_3^{-2}$)	H_2S, HS^-, FeS
	Desulfoto-maculum	6 – 8	283.15 – 313.15		
	Desulfo-monas		(Some at 319.15 - 347.15)		

			283.15 – 313.15		
Acid-producing bacteria (Facultative)	*Clostridium aceticum*	<7		Organic compounds, hydrocarbons, O_2	Organic acids including formic acid (HCOOH) and acetic acid (CH_3COOH), CO_2
Sulfur-oxidizing bacteria (Aerobic)	*Acidithio-bacillus thiooxidans*	0.5–8	293.15 – 323.15	Sulfide, sulfite, thiosulfate and elemental sulfur Organic compounds, CO_2, O_2	Sulfuric acid (H_2SO_4), S^0
Iron-reducing bacteria (Facultative)	*Pseudomonas sp.*	4–9	294.15 – 313.15	Insoluble Ferric iron (Fe^{3+}), O_2, NO_3^-	Soluble Ferrous iron (Fe^{2+})
Iron/Manganese-oxidizing bacteria (Aerobic)	*Acidithio-bacillus ferrooxidans*	1–7	283.15 – 313.15	Ferrous iron (Fe^{2+}), Mn^{2+}	Ferric iron (Fe^{3+}), Mn^{4+}
	Gallionella	7–10			
	Leptothrix	6.5–9	294.15 – 313.15		
			283.15 – 308.15		
Nitrate-reducing bacteria (Facultative)	*Azonexus*	7 – 8	288.15 – 298.15	Organic compounds, NO_3^-, O_2	NO_2^-, N_2O, NO, N_2
Methanogens (Anaerobic)	*Methermicoccus*	5 – 6	310.15 – 358.15	Organic compounds, CO_2 (or soluble CO_3^{2-}, HCO_3^-, H_2CO_3) or H_2	Methane (CH_4), CO

Figure 2.3 shows the distribution of various groups of microorganisms based on their O_2 requirements along the depth of a typical biofilm.

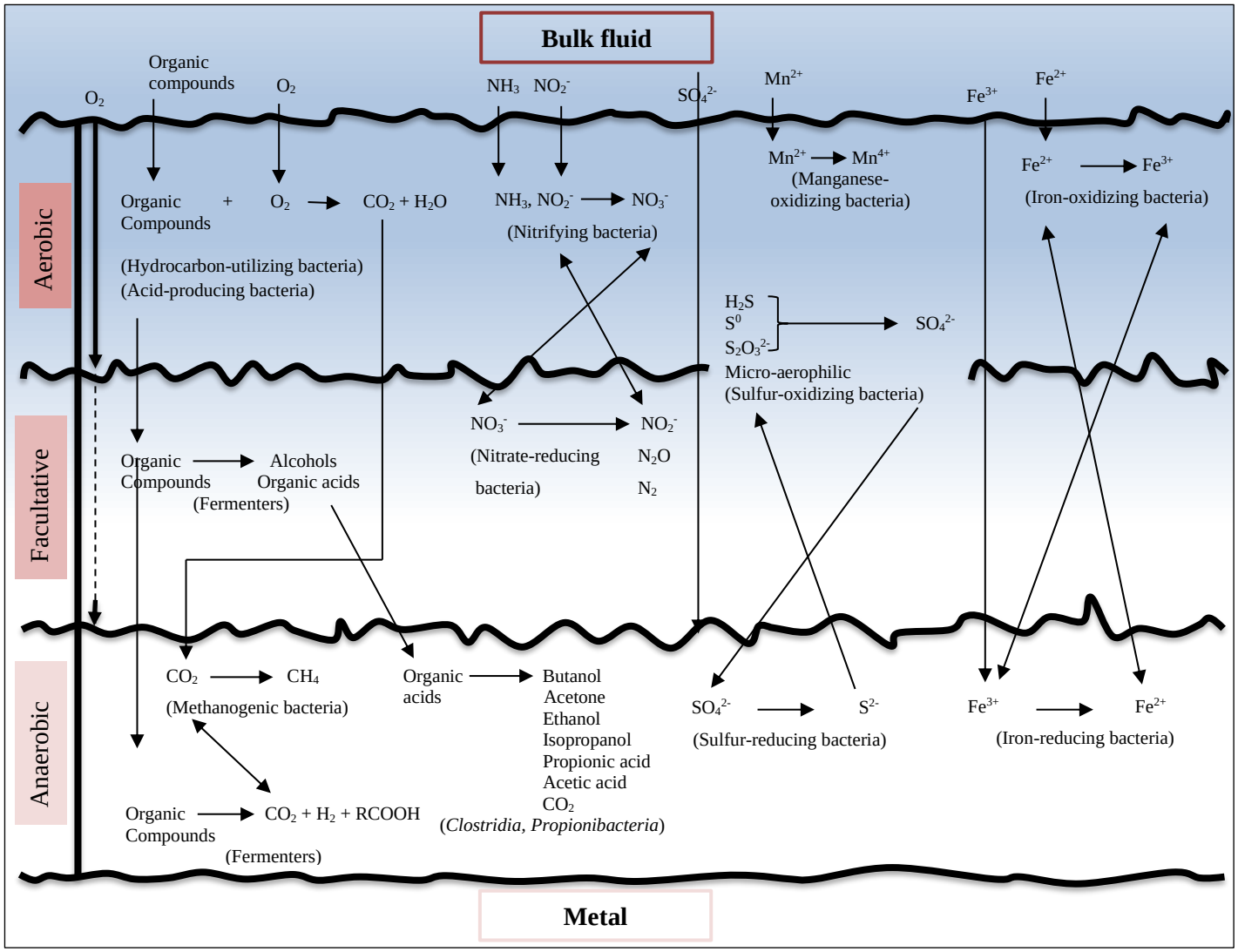

Figure 2.3: Distribution of microbes into anaerobe, facultative and aerobe, within a typical biofilm, adapted from [16] with modification.

MIC may be influenced by the various microbial processes in the biofilm resulting in different electrochemical reactions and producing metabolites with secondary effects. The

activity of one group of microbes may promote or inhibit the growth of the other group [47]. The biofilm is an open structure which allows transfer of nutrients to the metal surface. However, it may contain certain zones where the diffusion of chemical species (e.g. O_2) is limited as depicted in Figure 2.3. Biofilms can also incorporate electrochemical corrosion products such as oxide-based corrosion products, which can be utilized by the microbes or influence the surrounding chemistry [48]. Thus, there exist a complex interaction between the chemical/electrochemical process and MIC due to the overlapping consumption and production of chemical species.

2.4 Electrochemical Corrosion

Corrosion of metal is the physicochemical interaction between a metal and its environment caused by chemical or electrochemical reaction. This results in gradual deterioration of metal by refining its properties to a more stable energy state [49]. Metals exist naturally in a thermodynamically stable state as oxides, hydroxides, or sulfides. This makes corrosion to be a natural process that converts a refined metal to a more chemically stable compound, i.e. the corrosion products. The precursors of electrochemical corrosion are three essential components which must be present and interact with one another [29]. These are the anode (where oxidation reaction takes place), the cathode (where reduction reaction takes place) and the electrolyte (aqueous solution through which the positively and negatively charged ions flow).

For instance, metallic iron (Fe^0) undergoes oxidation to ferrous ion (Fe^{2+}) through loss of electron (eq. 11) at the anode. The metal dissolves into solution and causes the area of the metal surface to corrode [29].

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \text{(Eq. 11)}$$

At the cathode, the electron produced at the anode are consumed, causing reduction of electron acceptor compounds. For instance, O_2 is reduced in oxic environments at the cathode as described in eq. 12 and 13. The corrosion rate is relatively high under these conditions [37].

For acidic solution: $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$ (Eq. 12)

For neutral or basic solution: $O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$ (Eq. 13)

In anoxic conditions, reduction of hydrogen ion (H^+) to H_2 is a typical electron consuming reaction at the cathode (eq. 14), especially in acidic solutions. Electrons react with H^+ from the solution which are adsorbed on the metal surface [29].

$$2H^+ + 2e^- \leftrightarrow H_2 \quad \text{(Eq. 14)}$$

In theory, corrosion of iron in anoxic environments is less probable due to the slow reaction of H^+ reduction however, microbial activity is associated with iron corrosion under anoxic conditions [28,37]. Identification and quantification of the products of corrosion are important in MIC as they can impact microbial growth and also react with the compounds in the surrounding solution.

2.5 Corrosion Products

The formation of corrosion products (stoichiometric and non-stoichiometric compounds) depends on the physicochemical condition of the environment around the metal. For example, CO_2 corrosion of steel may produce iron carbonate ($FeCO_3$) and amorphous forms of cementite (Fe_3C) [50]. Amorphous forms of mackinawite $Fe_{(1+x)}S$), pyrite (FeS_2), and pyrrhotite ($Fe_{(1-x)}S$) are possible corrosion products associated with environments containing H_2S and other sulfur compounds [51]. Table 2.4 shows various corrosion products formed under different chemical environments.

Table 2.4: Examples of corrosion products as a function of redox environment.

Redox environment	Corrosion product	Composition	References
Oxic environment (O_2)	Iron (II) hydroxide	$Fe(OH)_2$ or $FeO.nH_2O$	[52–54]
	Ferrous oxide	FeO	
	Hematite (common rust)	$Fe(OH)_3$ or $Fe_2O_3.nH_2O$	
	Magnetite	Fe_3O_4 or $Fe_2O_3.FeO.nH_2O$	
	Goethite	α-FeOOH	
	Lepidocrocite	γ-FeOOH	
	Maghemite	γ-Fe_2O_3	
CO_2 environment	Siderite	$FeCO_3$	[50]
	Cementite (metastable carbide)	Fe_3C	
H_2S environment	Mackinawite (varies)	$Fe_{(1+x)}S$ (x = 0 - 1, e.g., Fe_9S_8)	[51,52,54]
	Pyrite (stable)	FeS_2	
	Troilite (stable)	FeS	
	Marcasite (metastable)	FeS_2	

Greigite (metastable)	Fe_3S_4
Pyrrhotite (metastable)	$Fe_{(1-x)}S$ (e.g., Fe_7S_8)
Smythite	Fe_9S_{11}
Ferrous sulfate	$FeSO_4$
Mikasaite	$Fe_2(SO_4)_3$

Studies have shown that layers of corrosion products on carbon steel can be protective to further corrosion [55,56]. Corrosive species are physically blocked from reaching the steel by the corrosion product layers. The protective deposit layer on the metal surface can break down in the presence of chloride ions (Cl^-), leading to rapid dissolution of the substrate metal [56,57]. In addition, metabolites from microbial activities such as organic acids and S^{2-} can destroy the protective corrosion product layer and promote hydrogen permeation [58]. Given that these same compounds can be produced and/or utilized by the microbes and present in the surrounding solution, identifying how these environments (solution, corrosion, and microbial) interact is key to understanding MIC. The environmental factors (e.g. surrounding solution chemistry) often impact microbial activities and will feed into the corrosion rate.

2.6 Environmental Factors Influencing Corrosion

Several environmental factors affect corrosion rate in oil and gas facilities including temperature, pressure, pH, flow, oil phase composition, gas-phase composition (e.g. O_2, H_2S, CO_2, SO_x, NO_x, and NH_3), aqueous phase composition (salts and organic acids in

produced water) and solids [54] etc. The microbial activities are a function of the surrounding environment.

2.6.1 Flow

Flow can remove corrosion products from the metal surface or enhance contact between corrosive species such as dissolved O_2 and the metal surface [54]. Flow-induced localized corrosion (FILC) occurs due to increased mass transfer and turbulence of fluid flow over a surface [59]. Erosion and under-deposit corrosion influences corrosion through phase transfer in a two-phase system under high flow and low flow operating conditions respectively [54]. Fluid dynamics can also inhibit biofilm formation and impacts corrosion on metal surface at high flows. In a study [60], biofilm is not able to form at high fluid velocity of 1.0 m/s. However, at 0.2 m/s fluid velocity, a layer of biofilm was observed which led to MIC. The corrosion products and biofilm form as the surface layer at low flow rates, while at high flow rate only corrosion products dominate. Fluid flow can also impact microbial growth in the biofilm by limiting oxygen availability and lower the diffusive exchange of nutrients in the biofilm [61,62].

2.6.2 Sulfides ($H_2S/HS^-/S^{2-}$)

Carbon steel and alloys are susceptible to H_2S corrosion and sulfide stress cracking (SSC) in H_2S-containing systems (sour environments) [63]. Sulfur and sulfides may exist naturally in oil and gas flow lines or produced by the microbial activity of SRB. H_2S dissolves in aqueous phase to form a weak acid. The solubility of H_2S in water in saline solutions (NaCl) decreases with increase in temperature at pressures less than 4.0×10^3 kPa

and partition to the gas phase. However, at pressures greater than 1.4 x 10^4 kPa, the solubility increases with increase in temperature [64–66]. Under atmospheric conditions, the pH of water-H_2S system at equilibrium reaches a value of ~4 in the absence of buffering ions and can drop to 3 at higher pressures [67]. At a pH 5 – 9, a mixture of dissolved H_2S and HS^- exist in the aqueous phase and HS^- specie predominates above pH 9. HS^- further dissociates into S^{2-} at higher pH and become the major specie at pH of 14 (eq. 15 – 17) [68,69].

$$H_2S(g) \rightarrow H_2S(aq) \quad \text{(Eq. 15)}$$

$$H_2S(aq) \rightarrow H^+(aq) + HS^-(aq) \quad \text{(Eq. 16)}$$

$$HS^-(aq) \rightarrow H^+(aq) + S^{2-}(aq) \quad \text{(Eq. 17)}$$

The solubility of elemental sulfur in water increases with temperature, from a concentration range of ~10 ppm – 20 ppm at 298.15 K to 50 ppm at 323.15 K. Sulfur reacts with water to produce H_2S and H_2SO_4, corrosive compounds for iron and carbon steel (eq. 18 and 19) [54,70].

$$4S + 4H_2O \rightarrow 3H_2S + H_2SO_4 \quad \text{(Eq. 18)}$$

$$Fe + H_2S \rightarrow FeS + H_2 \quad \text{(Eq. 19)}$$

H_2S is known to form a protective scale of iron sulfide (FeS) with different crystalline structures, which may have some inhibitory effect on further corrosion. However, the level of protection depends on conditions such as H_2S concentration or pH and temperature [71]. Polysulfides (S_n^{2-}) are typically corrosive sulfur intermediates similar to SO_3^{-2}, and

bisulfite (HSO_3^-) [72]. The sulfide produced by SRBs can be oxidized further to corrosive elemental sulfur, thiosulfate and polysulfide by soNRB due to O_2 ingress or nitrate amendment [73]. H_2S has also been found to inhibit the sulfate reduction activity of SRB at 547 mg/L concentration due to toxicity effect. This inhibition may be reversible as H_2S concentration drops [74].

2.6.3 Carbon dioxide (CO_2)

CO_2 solubility in water at 100 kPa varies from 265 – 320 ppm at 20°C to 1125 – 1400 ppm at 80°C [75]. CO_2 can react with water to form carbonic acid (H_2CO_3) [76]. In a CO_2 environment, H_2CO_3 dissociates into bicarbonate (HCO_3^-) which dominates within the pH range of 6 – 10, and carbonate (CO_3^{2-}) at pH above 10. The following reactions (eq. 20 – 23) have been proposed for the corrosion of carbon steel in CO_2 environment [77].

$$Fe + 2\,H_2CO_3 \rightarrow Fe(HCO_3)_2 + H_2 \quad \text{(Eq. 20)}$$

$$Fe(HCO_3)_2 \rightarrow Fe^{2+} + 2HCO_3^- \quad \text{(Eq. 21)}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad \text{(Eq. 22)}$$

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \quad \text{(Eq. 23)}$$

The corrosion products ($Fe(HCO_3)_2$ and $FeCO_3$) form a tightly attached layer over the metal surface and reduces the corrosion rate [77,78]. However, the degree of protection depends on pH, temperature, velocity, H_2S, and steel type [54]. Other secondary reaction products may form including iron oxides or hydroxides. After long exposures, the

corrosion products layer may become non-adherent and porous, causing localized pitting corrosion to occur.

Some groups of MIC microorganisms such as Methanogens and SOB derive carbon from CO_2 for growth. Other groups including APB and Fermenters produce CO_2 as metabolite. As such, the microbial activity influences the overall concentration of CO_2 in the environment.

2.6.4 Oxygen (O_2)

Oxygen plays a major role in corrosion of oil and gas facilities [54,79]. Only trace amounts (ppm levels) of O_2 are required for corrosion to occur (see Figure 2.4), [80].

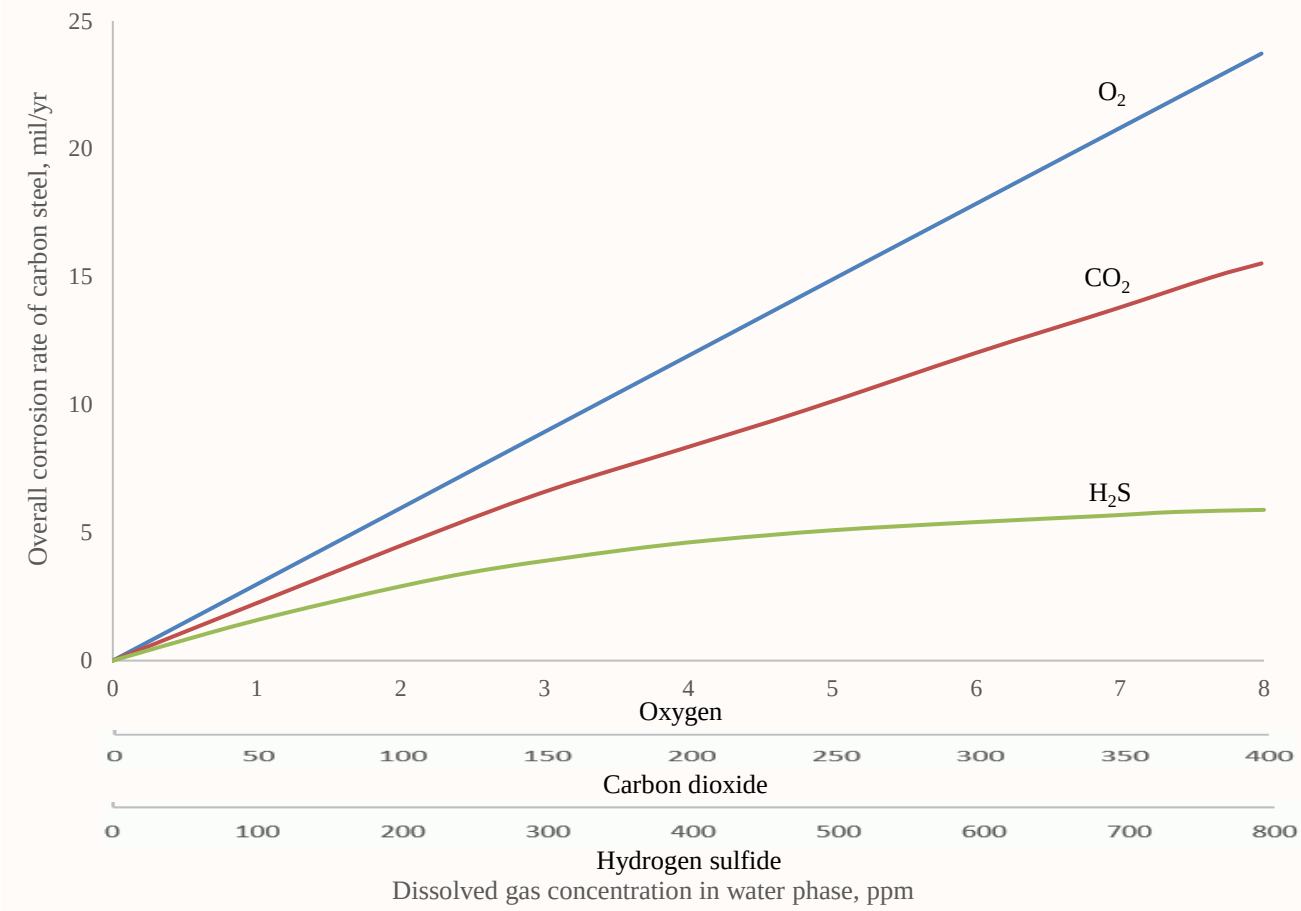

Figure 2.4: Comparison of corrosion rates of steel in the presence of H_2S, CO_2, and O_2, adapted from [79].

As indicated in Figure 2.4, O_2 is 50 times more corrosive than CO_2 and 100 times more corrosive than H_2S. The presence of O_2 increases the corrosive effects of the acid gases (CO_2 and H_2S) on iron and carbon steel [79].The O_2 reduction at the cathode depends on the pH of the medium (eq. 12 and 13) and has a relatively fast kinetics. Iron or carbon steel in the presence of O_2 can form a porous layer of ferrous hydroxide ($Fe(OH)_2$) and further oxidation yields a reddish-brown ferric hydroxide ($Fe(OH)_3$), (eq. 24 and 25)

$$Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2 \qquad \text{(Eq. 24)}$$

$$Fe(OH)_2 + \frac{1}{2}H_2O + \frac{1}{4}O_2 \rightarrow Fe(OH)_3 \quad \text{(Eq. 25)}$$

A black hydrous ferrous-ferrite oxide (magnetite) may be formed as an intermediate product. The adherence and compactness of the corrosion products as protective layers depend on pH level and Cl^- concentration. [56].

Microorganisms vary in their requirements for molecular O_2. Aerobes utilize O_2 as a terminal electron acceptor for respiration while anaerobes cannot grow in the presence of oxygen. The APB, IOB, and SOB are typical examples of MIC-related aerobic microbes. Having described the important role of O_2 on corrosion, aerobic microorganisms may help to remove O_2 (corrosive agents) through physiological activities. The O_2 utilization may however be at the expense of producing other corrosive metabolites resulting in MIC.

2.6.5 Temperature

The corrosion rate doubles for every 10 to 15 K rise in temperature within the range of 273.15 – 348.15 K. The effect of temperature on corrosion rate may be accelerated in an acidic medium [81]. At a constant H_2S concentration, the corrosion rate increases with temperature from 278.15 – 333.15 K and independent of the temperature between 363.15 and 423.15 K. The protective surface layer formed is hard and adherent at approximately 423.15 K [54,82]. Table 2.5 summarizes the effects of temperature on corrosion rates in different environments.

Table 2.5: Summary of the temperature effects on corrosion rates of carbon steel [54,81–84].

	Temperature range	Corrosion rate impact
H_2S	278.15 – 333.15 K	Corrosion rate increases
	363.15 – 423.15 K	No significant effect on corrosion rate
	423.15 K	Corrosion rate slows down due to very hard and adherent surface layer
	493.15 K	Corrosion rate decrease further. Pyrrhotite predominate, with small amounts of pyrite and troilite
CO_2	Below 293.15 K	Corrosion rate increases. No formation of $FeCO_3$ surface layer
	293.15 – 313.15 K	No significant effect on corrosion rate. Surface layers are not adherent and may be removed easily
	313.15 – 333.15 K	Corrosion rate slows down. Surface layers formed are protective
	333.15 – 423.15 K	No further corrosion. Surface layers are hard, adherent, and protective
O_2	For every 30 degrees rise in temperature	Corrosion rate of carbon steel doubles
	Open system	Corrosion rate drops at the boiling point due to the evaporation of water (disappearance of dissolved O_2)
	Closed system	Corrosion rate continues to increase with temperature

Figure 2.5 summarizes the relationship between temperature and corrosion rate of iron in an open and closed system containing dissolved O_2. In an open or flow system, the corrosion rate increases with temperature and drops towards the boiling point of water. The corrosion rate increases with temperature in a closed system as the O_2 remains in the system [54].

MIC-associated microbes respond differently to temperature, for instance, the optimum temperature for SRB growth is ~298.15 K but can still survive at 333.15 K [85]. Most of

the dominant MIC microbes fall in the categories of mesophiles (293.15 - 318.15 K). Other few ones such as Methanogens have wider temperature range and can thrive in the thermophilic region (318.15 - 395.15 K).

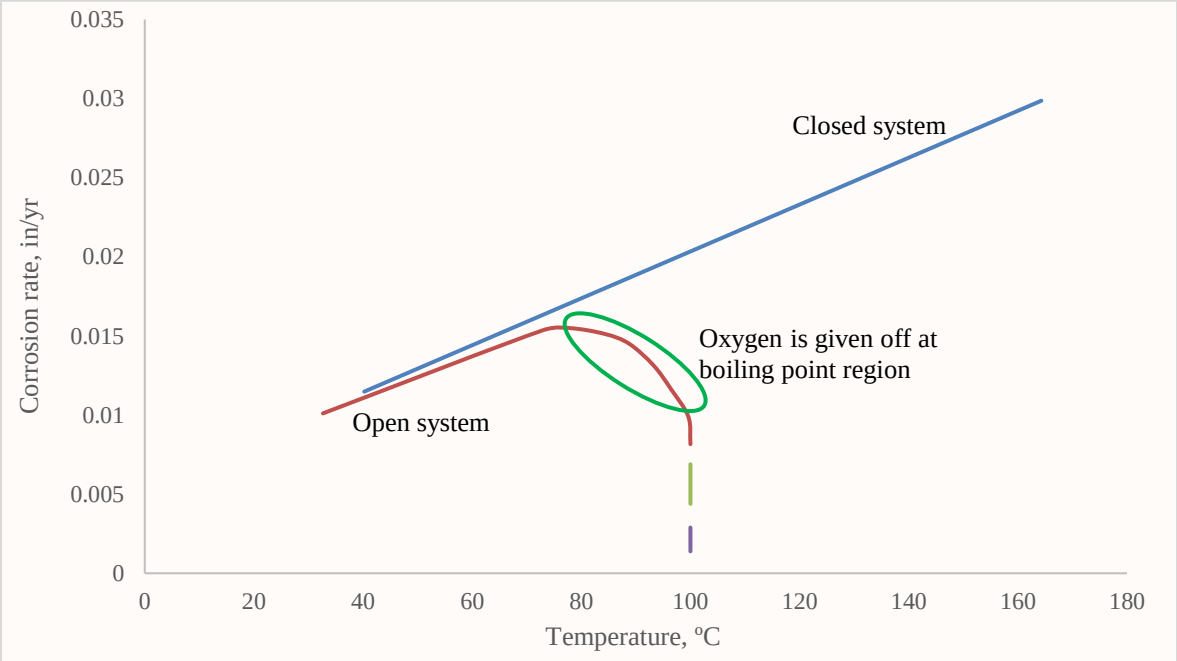

Figure 2.5: Effect of temperature on corrosion rates of iron steel in water containing dissolved O_2, adapted from [84]

2.6.6 Pressure

The effect of pressure on corrosion depends on the partial pressures of acid gases (e.g. H_2S, polysulfide, and CO_2), which may influence the dissolution of corrosive species into the solution. Higher pressures may also increase corrosion rate by enhancing the dissolution of the protective surface layer from the metal surface. However, higher pressures may

facilitate the formation of adherent and compact surface layer and therefore decrease corrosion [54].

Microbial growth/activity is proposed to occur over a wide range of pressure [86]. For example, SRB can tolerate up to 5.06 x 10^4 kPa pressure. A study [87] revealed that the application of negative pressure may slow down the microbial growth rate and inhibit biofilm development.

2.6.7 pH

In general, the pH of the aqueous phase in the oil and gas streams depends on the partial pressures of the CO_2 and H_2S. Other factors that may impact the pH level include temperature, organic acids (acetic acid), concentrations of buffering species such as acetate ions and bicarbonate, and concentration of scale-forming species e.g. calcium carbonate. Table 2.6 summarizes the impact of pH in the aqueous phase [54,88].

Table 2.6: Effects of some factors on pH, [88].

Parameter	Parameter Range	pH Range	Effect of increasing value of the parameter on pH
CO_2	68.95 – 551.58 kPa	4.5 – 5.5	Decreases
H_2S	68.95 – 551.58 kPa	4.8 – 5.5	Decreases
CO_2 and H_2S	551.58 kPa each	4.0 – 5.0	Same as for individual acid gases
Temperature	303.15 and 323.15 K	4.4 – 4.8	Slightly increases
$NaHCO_3$	4000 ppm	6.0	Increases and stabilizes (buffering)
CH_3COONa	4000 ppm	6.0	Increases and stabilizes (buffering)
CH_3COOH	4000 ppm	4.0	Decreases

A mixture of $NaHCO_3$ and CH_3COONa	4000 ppm each	6.0	Stabilizes (buffering)

In fluids with H_2S, highly acidic systems (pH 1.7 – 2.7) show no FeS layer formed at the surface, instead corrosion of iron takes place continuously and Fe^{2+} dissolves into the solution [89]. Surface layers in a CO_2 environment are formed and are stable at a minimum pH of 4.2 to 6.0. The pH range is a function of the dominant chemical species in the system (CO_2, carbonate, and bicarbonate), temperature, and flow rate [90]. For systems with high dissolved O_2 and pH less than 4, surface layers do not form, and the concentration has no effect on the corrosion rate. Between pH 4 to 10, the corrosion rate increases with increasing O_2 concentration. At above pH 10, the surface layers formed become very stable and compact, and thus, corrosion rate decreases [54].

pH influences microbial growth and activity; microorganisms have a preferred pH range for optimum growth. pH may have an inhibitory effect on microbial activity outside the optimum range. For instance, the SOB thrives at 0.5–8 pH range [32]. A more alkaline environment can retard its growth or cause complete inhibition (see table 2.3).

2.6.8 Oil phase composition

Crude oil is not inherently corrosive due to its low conductivity [91,92]. The corrosivity of crude oil depends on its chemical and physical constituents, chemicals partition between oil and aqueous phase, temperature, emulsion type, and wettability. Some chemical and physical constituents of crude oil which impact corrosivity include inorganic salts, sulfur contents, organic acids, dissolved gases, solids, and paraffin [54].

Inorganic salts can produce hydrogen chloride (HCl) at high temperatures, crude may contain 100–2000 mg/L of inorganic salts [93]. The sulfur content of crude oil is usually less than 1% and 2.0–3.5% for heavier crude [94]. The total sulfur is not the controlling factor for corrosion, but rather the degree of transformation of the sulfur compounds in the oil to more corrosive compounds including H_2S and HCl [95]. Sulfur compounds may provide corrosion resistance when stable sulfide layer is formed on the metal surface.

Naphthenic acid is the most important organic acids that contribute to crude oil corrosivity when the boiling point distillation temperature is high [92]. Corrosion has been recorded in the vacuum units of refineries at 493.15 – 643.15 K due to the presence of naphthenic acid. Carbon steel and stainless steels are vulnerable to naphthenic acid [54]. Other organic acids that may also influence corrosion at low temperatures include formic, acetic, and propionic acids [96]. Organic acids supply hydrogen ions (eq. 26) in the aqueous phase in contact with crude oil for cathodic reactions during the corrosion process [54].

$$\text{Acetic acid:} \quad CH_3COOH \longrightarrow CH_3COO^- + H^+ \qquad \text{(Eq. 26)}$$

The main corrosive gases are O_2, H_2S and CO_2. H_2S is more soluble in hydrocarbons than in water and has a saturation concentration of 5000 ppm in crude oil [97]. Both O_2 and CO_2 are also less soluble in water than in hydrocarbons [98].

Crude oil may contain finely divided particles of siliceous matter from solids and sediments. These particles may settle at the bottom of the pipe at low flow velocities and facilitate the occurrence of under-deposit corrosion, the extent depends on the amount and

composition of the solid deposits [98]. Paraffin tends to protect the pipe wall from corrosion by forming a layer on it. However, localized corrosion may occur when the layer entraps water [54].

The crude oil is a source of organic substrates or carbon for microorganisms, and the composition can impact the rate and type of microbial growth. Organic compounds are often utilized by both aerobic and anaerobic microorganisms (hydrocarbon-utilizing bacteria, APB, fermenters, and methanogens etc.) and are degraded to form organic acid, alcohol and/or CO_2 which may impact MIC.

2.6.9 Water (Aqueous) phase

Production water is the aqueous liquid phase produced with the oil and/or gas phases and can be a mixture of injection water, formation water (water present in the pores of hydrocarbon-producing rock layers) and/or condensed waters (water vapour in the reservoir fluids that condenses upon sufficient drop in pressure, temperature, or both), in various combinations and salinities. It is often referred to as brine due to high content of dissolved inorganic salts compared to typical seawater [99]. The corrosivity of water depends on the nature and concentration of ionic species present (anions and cations), the ions increase water conductivity, electrochemical reactions, and impact the properties of surface layers [54]. For instance, the dissociation of NaCl into Na^+ and Cl^- enhances the conductivity of water and stimulates transport of ions to and from the metal. Dissolved O_2 can form hydroxyl ions (OH^-) and undergo reduction reaction at the cathode (eq. 12 & 13).

It is an electron acceptor in the corrosion of iron as well as oxidation of ferrous iron. Cl^- can degrade oxide film layers at the metal surface leading to localized pitting corrosion.

The rate of pit development increases with increase in Cl^- concentration in the range 10,000 to 120,000 ppm [100]. Other halides may also impact pitting corrosion, however to a lesser degree. The order of the effect of halides on localized pitting corrosion is as follows [101]:

$$Cl^- > Br^- > I^- > F^-$$

Figure 2.6 illustrates the impact of increasing Cl^- concentration on the corrosion rate of iron in aerated solution at room temperature [102].

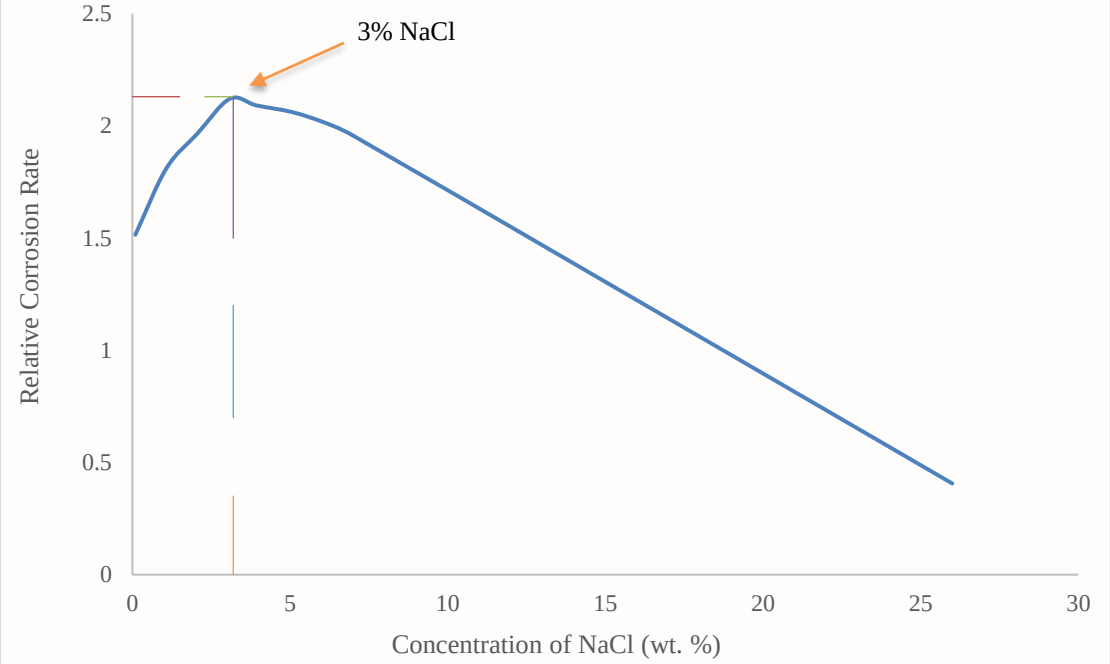

Figure 2.6: Variation in corrosion rate of iron in air-saturated distilled water at room temperature as a function of Cl ion concentration (added in the form of NaCl), adapted from [102].

Corrosion rate is a function of water conductivity. Increase in Cl^- concentration increases the water conductivity. Distilled pure water has the highest O_2 solubility but low conductivity. Addition of NaCl increases the corrosivity of the medium until 3% Cl^- concentration above which water corrosivity decreases. The higher the salinity, the lower the O_2 solubility. Thus, the corrosion rate decreases [103,104].

Conversely, phosphate ions decrease the susceptibility of metal to localized pitting as follows [101]. The most substituted phosphate ion with H^+ has the fastest impact towards pit initiation on metal:

$$H_2PO_4^- > HPO_4^{2-} > PO_4^{3-}$$

The effect of the cations on pit initiation was investigated and, all univalent cations including Na^+, K^+, Rb^+, and Cs^+ (excluding Li^+), increase the susceptibility of iron and steel to pitting corrosion [101]. The overall impact decreases as the size of the cation increases. Among the bivalent cations only Zn^{2+} increases the susceptibility of pitting corrosion, due to the hydrolysis of Zn salt which leads to low pH of the solution.

Cations and anions in aqueous phase can combine to form salt precipitate or scale. Scale formation may cause under-deposit corrosion and plug flowlines and process equipment. Examples of scale-forming compounds common in oil and gas operations include calcite (calcium carbonate ($CaCO_3$)) (eq. 27 and 28), calcium sulfate ($CaSO_4$), strontium sulfate ($SrSO_4$), and barium sulfate ($BaSO_4$). Scale formation depends on the solubility of the salt formed in the aqueous phase which in turn depends on temperature, pressure, and pH [54].

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad \text{(Eq. 27)}$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \quad \text{(Eq. 28)}$$

The saturation index (SI) can be used to determine the tendency of scale formation as shown in the following expression (eq. 29 and 30).

$$SI = \log_{10}(SR) \quad \text{(Eq. 29)}$$

$$SR = \frac{[\text{cation}] \cdot [\text{anion}]}{[\text{cation}]_{\text{satn.}} \cdot [\text{anion}]_{\text{satn.}}} \quad \text{(Eq. 30)}$$

SR (saturation ratio) is the ratio of the given concentration of ionic product to that under saturation conditions. For a solution containing a given salt, if SR is equal or greater than 1, the solution is saturated or supersaturated and scale may form; if SR is less than 1, the solution is undersaturated and scale may not form. Precipitation is a kinetically driven process, scale may not necessarily form even when SR is greater than 1 [54].

The aqueous phase provides the source of many essential microbial nutrients required for microbial growth and sink for microbial metabolites. These nutrients may exist in solution in ionic form (SO_4^{2-}, NO_3^-, PO_4^{3-}, CO_3^{2-} etc.) and are utilized as electron donor or acceptor to grow or generate energy for metabolism. Depending on the microbial group present in the system, some chemical species in the aqueous phase may inhibit growth or hinder microbial activity. A typical example is the nitrate inhibition of SRB.

2.7 Produced water composition

Produced water is a complex mixture of dissolved and particulate organic and inorganic chemicals in various proportions. The physical and chemical properties of produced water vary widely from one region to another and depend on reservoir depth, geologic age,

geochemistry of the hydrocarbon-bearing formation, chemical composition fluids in the reservoir, and production chemicals added during production operation [105]. The main components of the produced water stream are; dissolved organics (including hydrocarbons), dissolved minerals and gases (O_2, CO_2, H_2S), suspended oil (nonpolar) suspended solids (corrosion products, scale, sand, silt etc.), trace heavy metals, production chemicals (treating chemicals, kill fluids, acids, etc.), biomass [106]. Table 2.7 summarizes the inorganic constituents in produced water.

Table 2.7: Inorganic constituents in produced water

Compound/element/ion	References
Na, Ca, Mg, K, Sr, Ba, B, Li	[66,99,107–111]
NH_4^+, NH_3,	
$Cl^–$, $Br^–$, $I^–$	
$SO_4^{2–}$, $HSO_4^–$ $SO_3^{2–}$, $HSO_3^–$, S^0, H_2S, $HS^–$, $S^{2–}$, thiosulfate and polythionates species ($S_2O_3^{2–}$, $S_3O_6^{2–}$, $S_4O_6^{2–}$, $S_5O_6^{2–}$), polysulfide ($S_2^{2–}$, $S_3^{2–}$, $S_4^{2–}$, $S_5^{2–}$)	
$CO_3^{2–}$, $HCO_3^–$,	
dissolved O_2, $OH^–$,	
$NO_3^–$, $NO_2^–$, $PO_4^{3–}$	

Sulfur can also be present in produced water as a more oxidized form such as thiosulfate ($S_2O_3^{2–}$) and has long been known to cause localized corrosion. $S_2O_3^{2–}$ can be formed during microbial H_2S oxidation by SOB or chemical oxidation of H_2S following O_2 ingress. It is a metastable anion which can be oxidized or reduced, and can disproportionate or

decompose under different chemical and/or electrochemical conditions (see eq. 31−36) [110,112]. $S_2O_3^{2-}$ may oxidize to SO_3^{2-}, polythionates (e.g. trithionate, tetrathionate, and pentathionate), and/or to SO_4^{2-}, or reduce to S^0 and H_2S (or to polysulfides) [113]. The oxidation and reduction of $S_2O_3^{2-}$ can be mediated by SOB and SRB respectively. Polythionates have also been shown to follow similar reduction and/or disproportionation reactions causing corrosion of steel and stress corrosion cracking [114]. Thiosulfate is thermodynamically stable in neutral and alkaline solutions and expected to be more reactive with iron in low pH systems. Tetrathionate is relatively stable in acidic medium and more reactive at high pH [113]. Trithionate is relatively stable in non-oxidizing environments from acidic to basic conditions. SO_3^{2-} and HSO_3^- have commonly been used as O_2 scavengers to prevent O_2-related corrosion of carbon steel in systems where a limited amount of O_2 is present. These O_2 scavenger can act as a nutrient for SRB and influence microbial corrosion [115].

Oxidation:

$$2S_2O_3^{2-} + {}^1/_2\,O_2 + H_2O \rightarrow S_4O_6^{2-} + 2OH^- \quad \text{(Eq. 31)}$$

$$S_2O_3^{2-} + 2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + H_2O \quad \text{(Eq. 32)}$$

Reduction:

$$S_2O_3^{2-} + 6H^+ + 4e^- \rightarrow 2S + 3H_2O \quad \text{(Eq. 33)}$$

$$2S^0 + 4H^+ + 4e^- \rightarrow 2H_2S \quad \text{(Eq. 34)}$$

Disproportionation:

$$S_2O_3^{2-} + H^+ \rightarrow S^0 + HSO_3^- \quad \text{(Eq. 35)}$$

$$S_2O_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + S^{2-} + H_2O \quad \text{(Eq. 36)}$$

To mitigate the impact of sulfur in the form of H_2S, particularly reservoir souring, NO_3^- injection is a widely used method. NO_3^- stimulates the growth of NRB by consuming the limited nutrients within the reservoir and inhibit the growth and metabolism of SRBs. Introduction of NO_3^- may switch the metabolism of some SRBs to NO_3^- reduction due to the thermodynamic advantages involved with this reaction. NO_3^- and NO_2^- have inhibitory effect on the sulfate reduction activity of SRBs by competitively binding to the enzyme. The NRB can reduce NO_3^- and oxidize S^{2-} to SO_4^{2-} in the same redox reaction [73,116]. NO_2^- is an intermediary product of NO_3^- reduction from incomplete reduction. NO_2^- may play a dual role in corrosion as it is chemically corrosive due to its ability to oxidize iron and form ammonium [117]. Therefore, dosage is an important consideration when using nitrate as an SRB inhibitor, it should be sufficient to inhibit SRB activity and not so high to cause chemical steel corrosion by nitrite [73,118].

Produced water can contain organic acids, mono- and di-carboxylic acids (COOH) of saturated (aliphatic) and aromatic hydrocarbons. Low molecular weight carboxylic acids (formic, acetic, propanoic, butanoic, pentanoic, and hexanoic acids) [119], constitute most of the total organic carbon (TOC) in produced water [108]. Microorganisms such as bacteria and fungi utilize these low molecular weight organic acids as nutrients for metabolic activities. Organic acids are produced in the hydrocarbon-bearing formation through hydrous pyrolysis or microbial degradation of hydrocarbons [109].

2.8 Summary

This paper attempts to identify the major chemical species/compounds that contribute to MIC in oil and gas operations. Having reviewed various microorganisms associated with MIC (nutrients, metabolites, and growth conditions), surrounding chemical environment and chemical compounds resulting from different corrosive environments, several chemical species were identified to have potential impact on microbial activities which in turn leads to MIC. Table 2.8 summarizes these chemical species/compounds.

Table 2.8: Summary of chemical species associated with corrosion in oil and gas facilities

Microbial activities		**Chemical species present in the environment (e.g. produced water)**	**Corrosion products by electrochemical processes**
Utilized	**Produced**		
CO_2, organic compounds, organic acids, O_2, H_2, H_2O Soluble CO_3^{2-}, HCO_3^-, H_2CO_3	Organic acids (HCOOH, CH_3COOH), alcohols, CO_2, H_2O, H_2 CH_4, CO	Organic acids (HCOOH, CH_3COOH) Cl^-, Br^-, I^- Dissolved O_2, OH^- CO_3^{2-}, HCO_3^-	FeO, $Fe(OH)_2$, $Fe(OH)_3$ Fe_3O_4, γ-Fe_2O_3 α-FeOOH, γ-FeOOH $FeCO_3$, Fe_3C
NH_3, NO_2^-, N_2	NO_2^-, NO_3^-	NH_4^+, NH_3	
NO_3^-	NO_2^-, N_2O, NO, N_2, NH_4^+	NO_3^-, NO_2^-	

S^0, metal sulfide, H_2S, SO_3^{2-}, $S_2O_3^{2-}$ SO_4^{2-}	SO_4^{2-}, SO_3^{2-}, S^0 H_2S, HS^-, S^{2-}	SO_4^{2-}, HSO_4^- SO_3^{2-}, HSO_3^-, S^0, H_2S, HS^-, S^{2-}, thiosulfate ($S_2O_3^{2-}$) polythionates ($S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$), polysulfide (S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-})	FeS, FeS_2 $FeSO_4$, $Fe_2(SO_4)_3$ Fe_7S_8, Fe_3S_4 Fe_9S_8, Fe_9S_{11}
Fe^{2+}, Mn^{2+} Fe^{3+}	Fe^{3+}, Mn^{4+} Fe^{2+}	Metallic ion/element (Na, Ca, Mg, K, Sr, Ba, B, Li)	
PO_4^{3-}		PO_4^{3-}	

Given that the groups of microorganisms impacting MIC often co-exist in colonies and can enhance and/or inhibit their growth, understanding the chemistry of these environments is key. This perspective of MIC has not been covered in most recent studies of MIC. The interaction of microbial activities and chemical/electrochemical process makes MIC very different and more complex than chemical/electrochemical corrosion. This is due to the overlapping consumption and production of chemical species [48]. Figure 2.7 outlines the interaction between the chemical environment, environmental factors, and electrochemical processes with respect to microbial activities causing MIC.

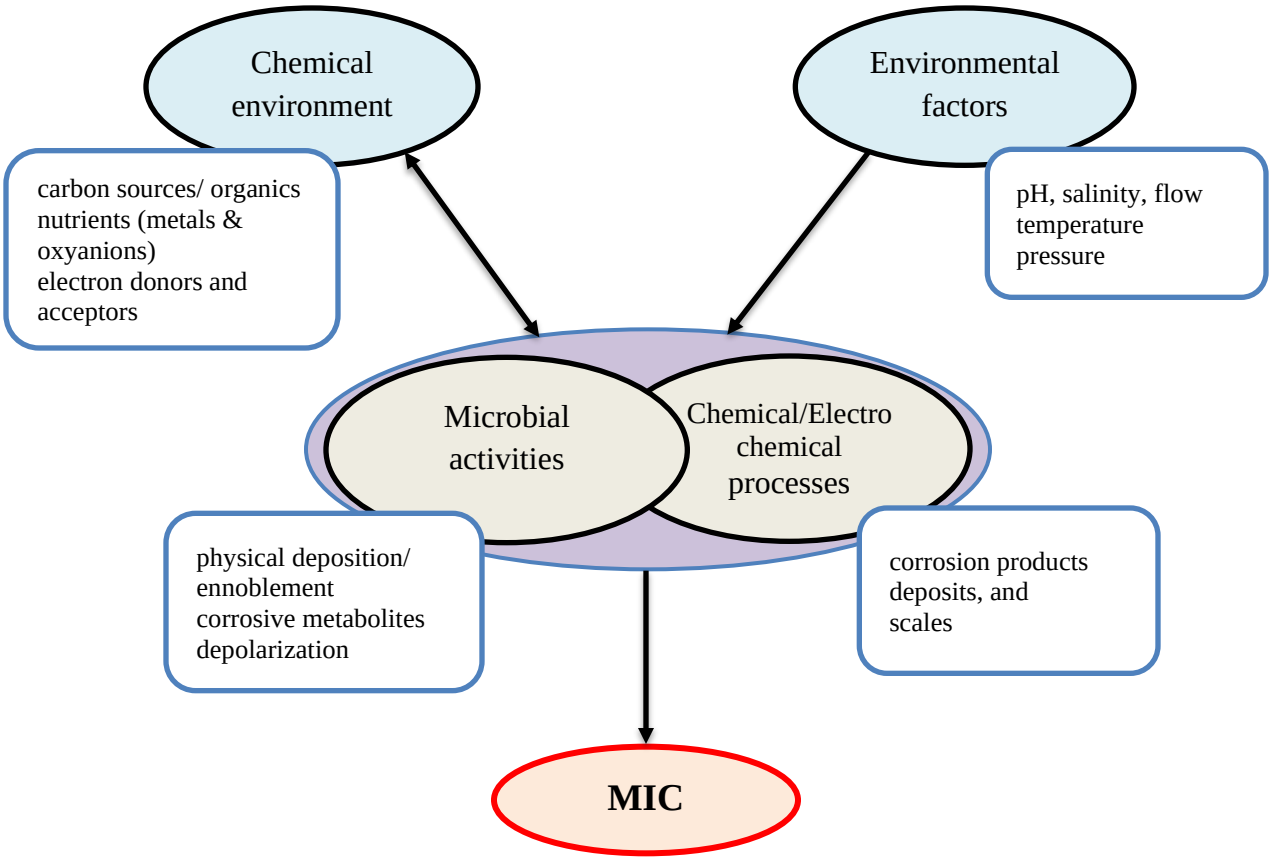

Figure 2.7: An outline of the interactions between chemical environment, environmental factors, electrochemical, and microbial processes.

For instance, as noted in previous sections the protective layers of corrosion products from electrochemical process may shield the metal surface from direct contact of biofilm deposition. However, corrosive microbial by-products including organic acids and S^{2-} may destroy the protective corrosion product layer and expose the metal surface to further corrosion due to microbial activities and/or electrochemical processes [58]. $Fe(OH)_3$ deposits serve as oxygen carrier and energy source for some bacteria [17]. A conductive FeS film may also serve in electron transport during iron reduction by IRB [120].

In general, the factors that influence MIC arise from both biotic and abiotic reactions occurring simultaneously, and difficult to distinguish the relative contributions of each for corrosion diagnosis. Chemical species may be co-currently or counter-currently consumed/produced through microbial activities and/or chemical reaction as depicted in Figure 2.8. MIC-related microorganisms thrive by metabolizing nutrients to excrete chemical species to the surrounding when favorable environmental conditions are met. Similarly, various chemical reactions may proceed at suitable conditions causing transformation of chemical species from one form to the other.

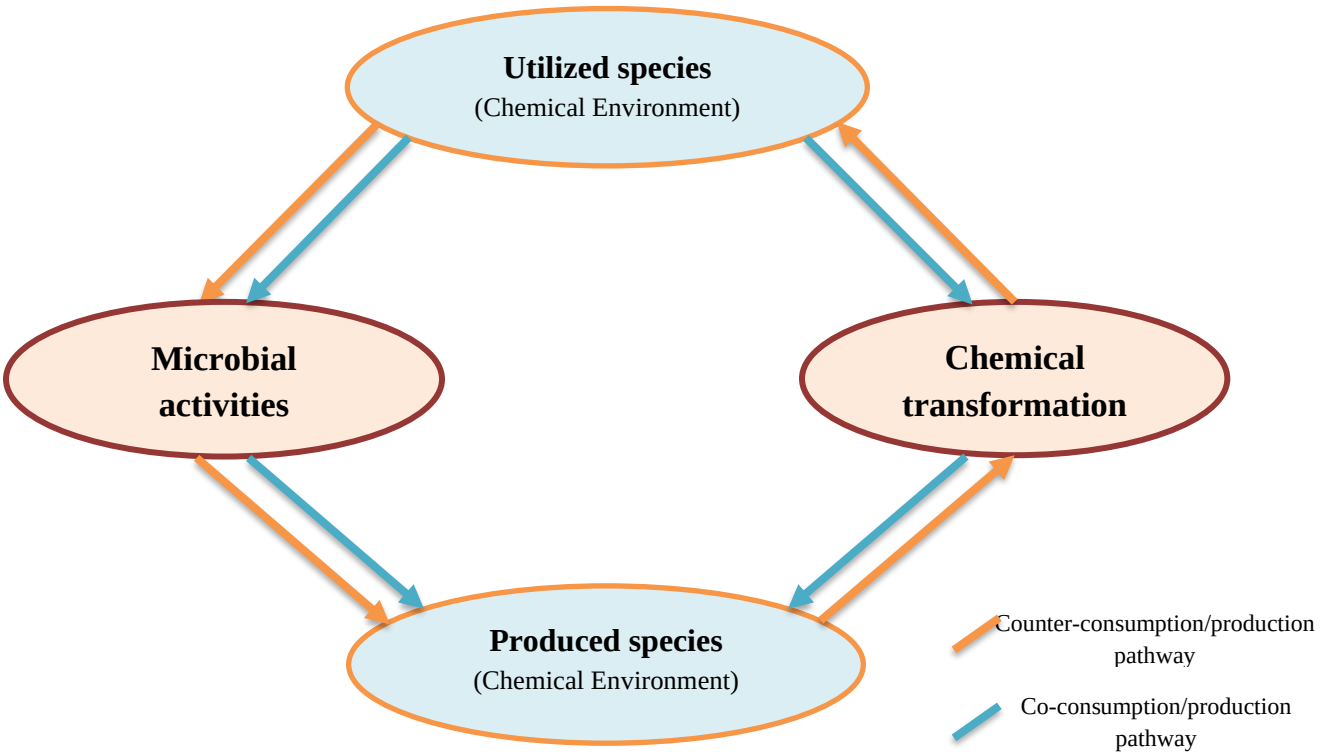

Figure 2.8: Schematic diagram showing the co-utilization/production and counter-utilization/production of chemical species in the environment via microbial activities and chemical transformation.

A possible instance of co-consumption/production of chemical species is the chemical reduction of $S_2O_3^{2-}$ to produce H_2S in an acidic medium as proposed by Tsujikawa, 1993 [121,122] (see eq. 33 and 34). Several SRB can also reduce $S_2O_3^{2-}$ to produce H_2S. In a case where $S_2O_3^{2-}$ and H_2S is being consumed and produced respectively via chemical and microbial mediated reactions simultaneously, the source of the corrosive species and/or relative contribution of each pathways may be difficult to identify and hence, wrong corrosion diagnosis.

On the hand, the counter-consumption/production of chemical species may also occur. H_2S can be oxidized in presence of oxygen to yield SO_3^{2-}, $S_2O_3^{2-}$, and SO_4^{2-} as the major products [123,124]. These reactions can take place over a wide range of pH (4–10) and temperature (283.15– 318.15 K) (see eq. 37–39). When oxygen is depleted in the system, many SRB thrive and obtain energy by reducing SO_3^{-2}, $S_2O_3^{-2}$, and SO_4^{2-} to produce H_2S, hence forming a loop.

$$H_2S + 1.5O_2 \rightarrow SO_3^{2-} + 2H^+ \quad \text{(Eq. 37)}$$

$$SO_3^{2-} + 0.5O_2 \rightarrow SO_4^{2-} \quad \text{(Eq. 38)}$$

$$H_2S + SO_3^{2-} + 0.5O_2 \rightarrow S_2O_3^{2-} + H_2O \quad \text{(Eq. 39)}$$

2.9 Conclusions

MIC has been studied for decades and various mechanisms have been proposed. Many chemical species in the corrosive environments are yet to be identified as essential contributors, influencing, or inhibiting microbial activities leading to MIC. Little is known

about the impact of mixtures of chemical species in a given environment on microbial activities and the dynamic behavior of the chemical environment due to changing conditions (pH, temperature, pressure, composition). The understanding of the overlapping effect of microbial activities and chemical reactions as well as chemical/electrochemical corrosion processes is diffuse and requires a consolidation and integration of data. This includes the rate at which chemical species are consumed, generated, and/or transformed from one form to the other through microbial actions and/or chemical means. All these account for the information gaps which are vital in developing a robust MIC mechanism and risk models which in turn allows a better deployment of corrosion management strategies [125].

The chemical environment is an important factor to be considered in MIC propagation. It provides the source for various kinds of microbial nutrients, sink for microbial bye-products and suitable medium for transformation of the chemical species impacting microbial activities. Therefore, investigation of the transformation of chemical species due to chemical-microbial interaction in such an environment requires identifying the key chemical species in the system causing corrosion or impacting microbial activities, possible effect of various operating conditions on these species and consequences of transformation of the chemical species in the system.

In this work, the chemical environment that may impact MIC was reviewed in an effort to better understand and describe the chemistry of MIC in the oil and gas facilities. This environment constitutes the major chemical species utilized and produced by MIC-associated microbes, precursors and corrosion products of chemical/electrochemical

processes, and composition of the surrounding chemical environment that contribute to MIC in offshore/onshore oil and gas operations. In an attempt to describing the chemical-microbial interaction, this paper highlights the linkages between the chemical environment, environmental factors, and electrochemical processes with respect to microbial activities causing MIC.

An in-depth study of the environmental chemistry of MIC could be achieved by identifying more compounds with major contributions, interaction pathways and impacts. Combination of models and well-designed experiments could help to integrate the chemical environment with microbial activities and enhance the understanding.

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3 SIMULATION OF SOUR-OXIC-NITRITE CHEMICAL ENVIRONMENT IN THE OIL AND GAS FACILITIES

Preface

A version of this manuscript has been accepted and published in the Canadian Journal of Chemical Engineering. I am the primary author of this work. Along with me are the co-authors; Kelly Hawboldt, Christina Bottaro and Faisal Khan. I developed the conceptual model and conducted the literature review. I carried out the data collection, simulation, analysis, and visualization. I prepared the original draft of the manuscript and subsequently revised the manuscript based on the co-authors' feedback. The co-author Kelly Hawboldt supervised the work, helped in the concept development, reviewed, and edited the manuscript. The co-authors Christina Bottaro and Faisal Khan contributed to preparing, reviewing, and editing the manuscript.

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Abstract

The nature of the chemical environment in oil and gas fluids such as produced water (PW) and soured oil, or low oxygen environments plays a vital role in microbiologically influenced corrosion (MIC). H_2S and/or other forms of sulfur species in soured oils and PW are key factors in corrosion and growth of microorganisms. To mitigate reservoir souring and subsequent corrosion, nitrate is injected to displace sulfate-reducing bacteria with nitrate reducers. However, nitrates and the associated nitrogen species (e.g. nitrite) impact the chemistry and microbial activity, and hence the corrosion potential in the system. The current study investigates the PW chemical environment in light of sulfide and nitrite chemistry and provides information towards understanding the chemical transformations and microbial relationships. The sulfide-nitrite environment was studied as a function of temperature, pressure, nitrite level, and oxygen using equilibrium, and kinetic model approaches. The equilibrium simulation predicted the formation of FeS, $FeO(OH)$, and Fe_2O_3 as the key corrosion products, the amount of which varied depending on the chemistry and operating conditions. In experiments where nitrite was very low or absent, S^0 was favoured over SO_4^{2-} as the inlet H_2S concentration increased and FeS dominated with increase in temperature. In the presence of nitrite, Fe_2O_3 was formed instead of $FeO(OH)$ at temperatures above 50°C. The trend of the kinetic simulation of the sulfide-oxygen reaction in seawater was in good agreement with the wet-lab experiment in PW. The models can serve as tools to better understand and describe the chemical environment in PW systems.

Keywords: Equilibrium model, kinetic model, produced-water chemical environment, nitrite, sulfide.

3.1 Introduction

The production of sulfide and other sulfur species in reservoir fluids is referred to as souring, and souring can result in corrosion in addition to environmental and safety concerns. Sulfide ($H_2S/HS^-/S^{2-}$) can be produced in reservoirs through a number of paths depending on reservoir and production conditions, such as thermochemical sulfate reduction (TSR), aquathermolysis and/or microbial sulfate reduction (MSR) [1]. Iron bearing reservoirs, such as pyrite (FeS_2), siderite ($FeCO_3$), hematite (Fe_2O_3) and chlorites, have the ability to scavenge sulfide in soured reservoir fluids by reaction or adsorption on iron minerals [2]. MSR can be exacerbated by oil and gas recovery methods such as seawater flooding due to the high sulfate (SO_4^{2-}) content in seawater. Nitrate (NO_3^-)/nitrite (NO_2^-) injection has been used to mitigate reservoir souring in oil fields. However, recent studies proposed that NO_3^- injection can also lead to increased corrosion rate under certain conditions [2–9]. Since NO_3^-/NO_2^- and O_2 are both strong oxidants, they can shift the chemical redox potential of the system to increase the formation of corrosive elemental sulfur (S^0), and partially oxidized by-products including sulfite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$) [10].

Sulfur (S) and nitrogen (N) species exist in the marine environment in various states (oxidized, reduced, and intermediate) and shift according to pressure, temperature, pH, and other changes in the system via a complex network of competing chemical and biological reactions. Distinguishing chemical/electrochemical and microbial mediated processes from each other and understanding how they interact is a challenge, which is further complicated

by partitioning behavior of species in oil, water, and gas. These processes all impact corrosion (see Figure 3.1).

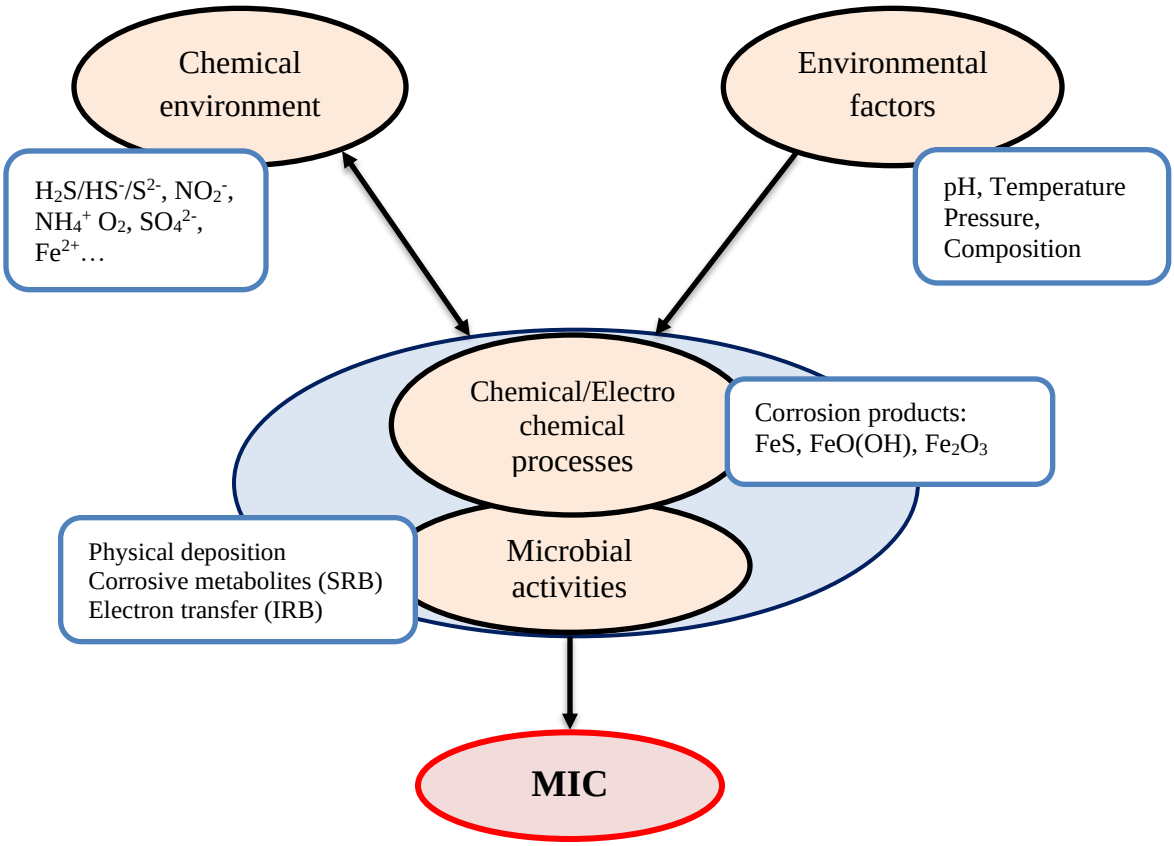

Figure 3.1: An outline of the problem: interactions between chemical environment, environmental factors, and chemical/microbial processes, adapted from [11] with modification

Little is known about the influence of sulfur and nitrogen species distributions and transformations in a given PW environment on microbial activities and the relative contribution of the chemical environment due to the changing operating conditions in the offshore oil and gas topside facilities (e.g. temperature, pressure and composition), such as high, medium and low pressure separators. The bulk of published work [7–9,12–16] have

considered different reactions independent of the chemical environment and dynamic behavior due to changing conditions. In addition, microbially mediated transformations have been studied theoretically and experimentally without considering the contribution of the chemically driven transformations [10,12,17–19]. In this work, equilibrium and kinetic models were used to simulate the chemistry of fluids in the topside separation process of an offshore oil and gas production platform, with the goal of using the simulation to better understand the behavior of sulfur and nitrogen species and impact on MIC in these systems. Particular focus was on soured systems where NO_3^-/NO_2^- treatment was ongoing (as a reservoir souring treatment process) or in systems where O_2 may be present. CO_2 environment and microbially mediated transformations were not considered in this current work. The simulation was done to analyze the overall S and N chemistry, as these species influence both microbial activities and electrochemical processes at the metal–environment interface. The ultimate goal is to couple this chemistry model with microbial and corrosion models to generate a more robust understanding of corrosion (chemical or MIC), which can be used for improved risk models for the offshore oil and gas topside separation process. The review section will discuss the potential chemical transformations of species involved in the Modeled environment.

The paper is organized as follows: the introduction highlights the overview of the S and N environment and implication of transformations in PW system, problem statement, objective, and the limitation of the study. The second section presents a review of the potential reactions related to the chemical environment under study. The third section discusses the equilibrium and kinetic modeling approaches, and experimental method

utilized in the work. The fourth section presents the outcome of the modeling studies and the wet lab validation of the kinetic model. The fifth section summarizes the outcome of the work and highlights the main conclusions.

3.2 Review

SO_4^{2-} is the most oxidized form of sulfur (+6), and it is found in abundance in seawater. Sulfur can exist in other oxidation states including partially oxidized sulfur species (e.g. SO_3^{2-}, $S_2O_3^{2-}$, and S^0 etc.) and sulfide, representing the most reduced sulfur species at a valence of −2 [14]. Sulfur intermediates play key roles in the biogeochemical cycling of carbon, iron, manganese, and trace metals. Transformations of sulfide via oxidation, reduction and/or disproportionation reactions form the basis of the sulfur cycle, which is driven by chemical and/or microbiological processes [14]. Reservoir fluids impacted by souring can be treated with NO_3^- and, as such, this study focused on the chemical process transformation of S and N species. Table 3.1 summarizes the products of reactions of reduced sulfur compounds with different oxidants in marine environments based on experimental studies conducted at circumneutral pH (pH: 6–8).

Table 3.1: Products of chemical oxidation of reduced sulfur compounds in the marine environment

S-specie	Oxidant	Products	pH	Temperature (ºC)	Reference
H_2S	O_2	SO_4^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, S_n^{2-}, S^0	4–10	10–45	[15,20]
	NO_2^-	S_n^{2-}, S^0, NH_4^+	6.8–7.3	58–60	[12,13]
	Mn(IV)	S^0, $S_2O_3^{2-}$, SO_4^{2-}	4–8.5	5–45	[16]

	Fe(III)	S^0, S_n^{2-}, $S_2O_3^{2-}$	4–8.5	5–45	[16,21]
S_n^{2-}	O_2	S^0, $S_2O_3^{2-}$	4–10	10–45	[20,22]
FeS	O_2	S^0, $S_2O_3^{2-}$, $S_nO_6^{2-}$, SO_4^{2-}	7	25	[14,23]
	Mn(IV)	S^0, SO_4^{2-}	8	20	[24]
FeS_2	O_2	$S_2O_3^{2-}$, $S_nO_6^{2-}$, SO_3^{2-}, SO_4^{2-}	2–9	25	[25]
	Mn(IV)	$S_2O_3^{2-}$, $S_nO_6^{2-}$, SO_4^{2-}	8	20	[24]

3.2.1 Oxic and anoxic oxidation of H_2S and FeS

In sour systems, O_2 can stimulate chemical oxidation of H_2S and FeS to produce corrosive sulfur compounds [26]. Sulfide can react with dissolved O_2 to produce SO_4^{2-} and various intermediates including S^0, polythionates (thiosulfate, trithionate, and tetrathionate), and SO_3^{2-} [15,20]. The rate of O_2−mediated oxidation of sulfide is strongly dependent on the system pH, temperature, and sulfide−oxygen ratio [15]. A simplified reaction mechanism is described in Equations (1)-(3),

$$HS^- + 1.5O_2 \xrightarrow{k_1} SO_3^{2-} + H^+ \quad (1)$$

$$SO_3^{2-} + 0.5O_2 \xrightarrow{k_2} SO_4^{2-} \quad (2)$$

$$HS^- + SO_3^{2-} + 0.5O_2 \xrightarrow{k_3} S_2O_3^{2-} + OH^- \quad (3)$$

where k_1 and k_3 are in $M^{-1.5}min^{-1}$, and k_2 is in $M^{-0.5}min^{-1}$, respectively.

These rate constants of sulfide oxidation in seawater at 45ºC have been correlated to pH as:

$$\ln k_1 = -4.71 + 0.914\text{pH} - 0.0289\text{pH}^2 \quad (4)$$

$$\ln k_2 = 3.87 + 1.51\text{pH} - 0.103\text{pH}^2 \quad (5)$$

$$\ln k_3 = -9.09 + 3.01\text{pH} - 0.177\text{pH}^2 \quad (6)$$

The rate of chemical oxidation increases in the presence of trace metals such as Fe, Cu, and Mn which in turn affects the quantity of products formed. S^0 and polysulfides (S_n^{2-}) can form in systems with a high sulfide–oxygen ratio (Equations (7) and (8)). S_n^{2-}may rapidly decompose to $S_2O_3^{2-}$ and S^0 due to its instability under oxic conditions. The S^0 formed can further react with SO_3^{2-} to generate $S_2O_3^{2-}$ (Equation (9)) [15,20,22].

$$2HS^- + O_2 \rightarrow \ 2S^0 \ + \ 2OH^- \quad (7)$$

$$S_n^0 + HS^- \rightarrow \ HS_{n+1}^- \quad (8)$$

$$S^0 + SO_3^{2-} \rightarrow \ S_2O_3^{2-} \quad (9)$$

Microorganisms such as sulfur-oxidizing bacteria (SOB) can also oxidize sulfide or sulfur intermediates in the presence of O_2 to produce SO_4^{2-}. Other sulfur intermediates may be formed microbially at extremely low O_2 levels and other environmental conditions such as temperature, pressure, and pH [27]. At low concentrations of sulfide and O_2, the rate of the chemical sulfide oxidation decreases, while the microbial oxidation rate stays high. Hence, the biological sulfide oxidation may outcompete the chemical sulfide oxidation [14,28].

In anoxic environments, the chemical oxidation of sulfide can occur in the presence of Mn(IV) oxides (Equation (10)) and Fe(III) oxides (Equation (11)) to produce S^0, mainly. However, $S_2O_3^{2-}$ and SO_4^{2-} become more prominent as MnO_2–H_2S ratio increases [16]. MnO_2 can also react with FeS and FeS_2 due to its strong oxidizing ability [14].

$$MnO_2 + HS^- + 3H^+ \rightarrow Mn^{2+} + S^0 + 2H_2O \quad (10)$$

$$2FeO(OH) + HS^- + 5H^+ \rightarrow 2Fe^{2+} + S^0 + 4H_2O \quad (11)$$

FeS layers may be formed in the presence of excess sulfide according to Equation (12). The iron in FeS precipitate can be oxidized to Fe(III) oxides and S^0 when exposed to air (Equation (13)) [26,29]. The FeS layer is conductive and serves as electron mediator between Fe^0 on metal surface and S^0 deposits, and accelerates Fe^0 dissolution [10]. The contact of S^0 with FeS layer on the metal surface can increase corrosion rates to greater than 20 mm/y [29].

$$2FeO(OH) + 3H_2S \rightarrow 2FeS + S^0 + 4H_2O \quad (12)$$

$$4FeS + 3O_2 + 2H_2O \rightarrow S^0 + FeO(OH) \quad (13)$$

S^0 is an important product in H_2S and FeS oxidation in oxic and anoxic sour environments which can lead to severe corrosion in susceptible systems [30,31].

3.2.2 Nitrate/Nitrite in soured systems

NO_3^- injection is one of the strategies to control souring in the oil and gas facilities [5,10,32]. NO_3^- treatment stimulates the activities of heterotrophic nitrate reducing bacteria

(hNRB) and sulfide-oxidizing, or nitrate-reducing bacteria (soNRB) to outcompete sulfate reducing bacteria (SRB) for electron donors, such as organics. It can also oxidize sulfide directly. The NO_2^- generated by nitrate-reducers inhibits SRB activities and suppresses sulfide production [5,10,33].

A study by Kaster et al, [12] reported that NO_3^- had no effect on H_2S production, whereas NO_2^- inhibited sulfate reduction and suppressed souring at 0.25 mM or higher. Chemical reactions of NO_3^- with H_2S have been reported to be kinetically unfavorable [14], whereas NO_2^- react with H_2S in sour systems to form S_n^{2-} which may precipitate as S^0 according to Equations (14) and (15) [12,13].

$$4HS^- + NO_2^- + 5H^+ \rightarrow HS - S - S - S^- + NH_4^+ + 2H_2O \quad (14)$$

$$HS - (S)_7 - S^- \rightarrow S_8 \downarrow + HS^- \quad (15)$$

In H_2S-containing systems, NO_2^- may play dual role in corrosion depending on temperature, pH and NO_2^-/Cl^- concentrations. NO_2^- has been observed to enhance corrosion at concentrations below 3.5 mM and inhibits above 10 mM [8,9]. High concentrations of NO_2^- (>10 mM) in sour systems will form a thin passivating layer of Fe_2O_3 which reduces corrosion potential (Equation (16)) [34]. The rate of corrosion due to NO_2^- may increase at low pH as the passivating layer becomes unstable at pH less than 6 [7,35].

$$2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow 2NO + Fe_2O_3 + H_2O \quad (16)$$

Furthermore, it has been reported [47,48] from thermodynamic analysis using the redox potentials that NO_3^- and NO_2^- reduction coupled with Fe oxidation can potentially yield

thermodynamically favorable conditions for both corrosion and microbial growth. NO_3^- and NO_2^- reduction have much higher reduction potentials than SO_4^{2-} reduction [47]. Therefore, the NO_3^- and NO_2^- dosage is an important consideration when using NO_3^-/NO_2^- as an SRB inhibitor, it should be sufficient to inhibit SRB activity and not so high to cause chemical steel corrosion by NO_2^-. NO_2^- has been reported to promote corrosion at concentrations <3.5 mM but protects at levels >10 mM [10,32].

3.2.3 Intermediate S species

Partially oxidized S species (intermediates) such as $S_2O_3^{2-}$ and S^0 may cause localized corrosion at metallic surfaces [36,37]. $S_2O_3^{2-}$ and S^0 are formed in sour systems during microbially mediated or chemical oxidation of H_2S due to O_2 ingress or NO_2^-. $S_2O_3^{2-}$ is metastable and its transformation strongly depends on the pH of the system. It can be oxidized to SO_3^{2-} or SO_4^{2-}, reduced to S^0 or H_2S or undergoes disproportionation reaction to form HS^- and SO_4^{2-} [36]. Corrosion is initiated upon the reduction of $S_2O_3^{2-}$ to S^0 (Equation (17)) through the flow of electrons derived from Fe^0, especially at acidic pH [38].

$$4S_2O_3^{2-} + 24H^+ + 16e^- \rightarrow S_8^0 + 12H_2O \quad (17)$$

Severe corrosion may be caused due to S^0 at temperatures below 95°C and atmospheric pressure [39]. When S^0 is in direct contact with the metal surface, corrosion is initiated by FeS catalyzed S^0 reduction. The conductive FeS layer allows the iron corrosion to proceed

autocatalytically and further accelerate Fe^0 dissolution. S_n^0 solubilizes as HS_{n+1}^- to form FeS with Fe^{2+} (Equations (18) and (19)) [29].

$$FeS + S_8^0 + H^+ \rightarrow Fe^{2+} + HS_9^- \quad (18)$$

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \quad (19)$$

Other important intermediate S species are the polythionates such as $S_3O_6^{2-}$ and $S_4O_6^{2-}$. Polythionates are outside the scope of this work but will be considered in future work due to role in sulfur speciation both chemically and microbially [37].

3.3 Modeling and Experimental Methods

In this work, a staged approach to model the chemical reactivity of oil/gas/water soured systems was used. An equilibrium simulation of the oil–PW system was conducted to identify important species in the system and study the transformation of chemical species with varying conditions such as initial concentration, temperature, and pressure. Given that the results of thermodynamic equilibrium are based on infinite time for reaction, a kinetic approach can be a better way of modeling such system [40]. However, there are limited kinetic data available for many of the principal chemical reactions. The kinetic model was applied to the sulfide oxidation reactions as in Equations (1)-(3). The kinetic model was validated with data from literature and wet lab experiments conducted using field samples in the laboratory [15]. Figure 3.2 shows the simulation approach.

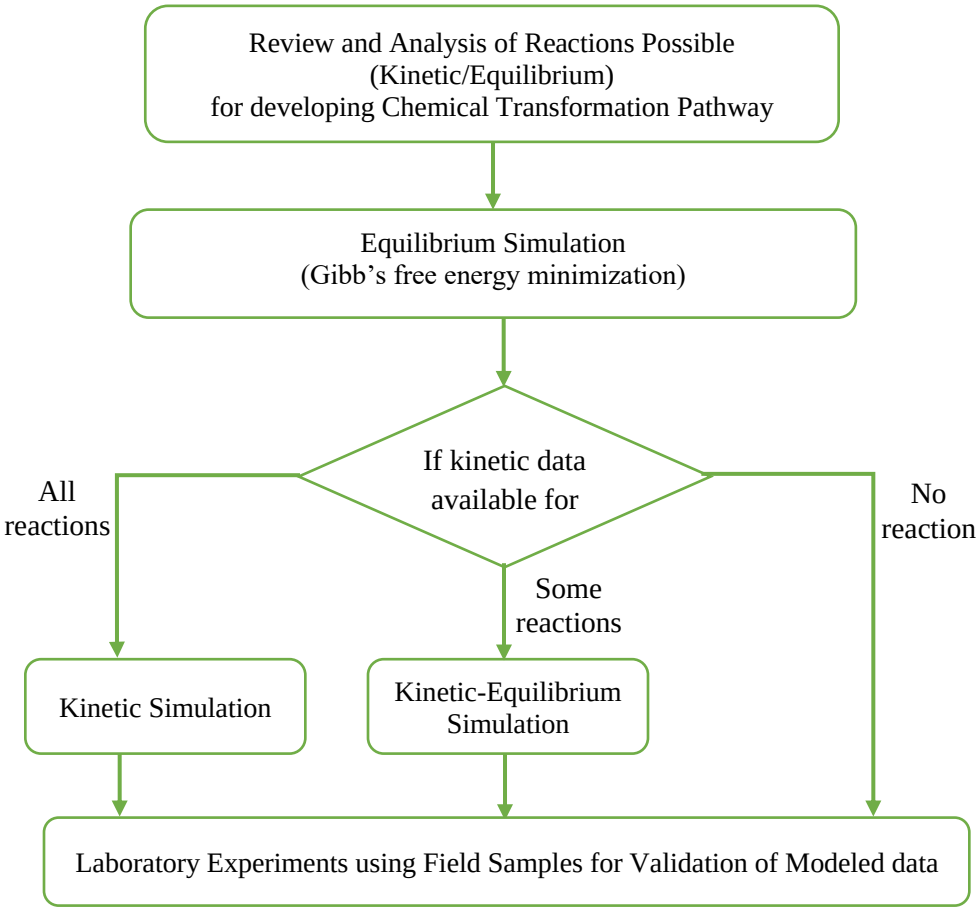

Figure 3.2: Algorithm for method development

3.3.1 Equilibrium Modeling

The Gibbs energy minimization approach was used for equilibrium calculations, where the species composition (n_i) that minimizes the objective function, G^t, for specified T and P, subject to constraints of conservation of total atomic masses in the system, is solved.

$$(G^t)_{T,P} = g(n_1, n_2, n_3, \ldots, n_N) \quad (20)$$

The material balance and equilibrium equation can be written as:

$$\sum_i n_i a_{ik} = A_k \; ; \qquad (k = 1, 2, \ldots, w) \tag{21}$$

$$\Delta G^o{}_{f_i,T} + RT \ln\left(y_i \widehat{\emptyset}_i \, P/P^o\right) + \sum_k \lambda_k a_{ik} = 0 \; ; \qquad (i = 1, 2, \ldots, N) \tag{22}$$

where A_k is the total number of atomic masses of the k^{th} element in the system, a_{ik} is the number of atoms of the k^{th} element present in each molecule of chemical species i, λ_k is the Lagrange multiplier and $\widehat{\emptyset}_i$ is the fugacity coefficient. Equation (21) is written for each element and Equation (22) is written for each chemical species to make a (N + w) system of non-linear equations. Detailed derivation can be found in Smith et al. [41]. This approach does not require an explicit determination of the set of independent chemical reactions that may be occurring in the system. However, it does require good initial guesses of amounts for better prediction.

The chemical equilibrium study was carried out using the equilibrium module of Outotec's HSC Chemistry Package 9. The HSC Chemistry 9 equilibrium module is incorporated with the Gibb's energy minimizer function as given in Equation (23) [42]:

$$G = \sum_j \sum_i n_i^j \left(g_i + RT \ln\left(\gamma_i \frac{n_i}{\sum_i n_i^j} \right) \right) \tag{23}$$

where j is the species phase, g_i is Gibb's energy of species i, R is the gas constant, T is the temperature, and γ_i is the activity coefficient of species i.

HSC Equilibrium module enables the calculation of multi-component equilibrium compositions in heterogeneous systems by specifying the chemical reaction system, phases

and species, and the amounts of raw materials. The program calculates the amounts of products at equilibrium as a function of temperature, pressure, and composition.

From previous work [11], a list of chemical species that may be present in a topside oil and gas produced fluid system were compiled. The PW compositions used for the equilibrium calculations were determined using data obtained from laboratory chemical analysis of field samples and the literature. The basis of the calculation was 1L of aqueous fluid which was equivalent to ~55.56 mol. Concentration data for sulfate, acetate, chloride, bromide, ammonium, and total iron were obtained from the laboratory measurements. The field- and laboratory-measured pH values of PW fell between 6–8. Table 3.2 presents a typical PW composition used for simulation.

Table 3.2: A typical PW composition adopted for simulation

Aqueous phase - Basis 1L	mg/L	mol/L
H_2O	1000000	55.56
H_2S	10	0.0003
H^+		0.0000001
SO_4^{2-}	2500	0.02604
CH_3COO^-	109.23	0.00185
Cl^-	25711.23	0.72426
Br^-	125.6	0.00157
HCO_3^-	142	0.00233
$NH4^+$	28.68	0.00159

Na^+	10760	0.46805
Ca^{2+}	416	0.01038
K^+	397.8	0.0102
Mg^{2+}	1283	0.0528
Total Fe	53.06	0.00095
Oil phase - Basis 1L		
Specific gravity	0.8554	
Normal boiling point (^{0}C)	147.7	

Table 3.3 outlines various input conditions considered for the equilibrium Modeling. Different combinations of the input conditions were simulated to study the chemistry of the system at equilibrium.

Table 3.3: Inlet conditions for equilibrium Modeling

Parameters	Low level	Intermediate level	High level
Temperature (^{0}C)	5	50	95
Pressure (Pa)	10^5	$1.5x10^6$	$3x10^6$
Oxygen (*Categoric*) (mM)	Anoxic – 0	-	Oxic (saturated) – 0.5
Nitrite level (mM)	0	6	12
Sulfide (mM)	0.2	0.6	1

3.3.2 Kinetic Modeling

Chemical equilibrium calculations assumes that a system has infinite time to reach final compositions. However in reality, the rates of reaction are critical for predicting the changes in chemical composition of the system over finite intervals.

To solve the kinetic equation, a simple mole balance for each component was used:

$$\frac{dC_i}{dt} = \sum_{m=1}^{R} \alpha_{im} r_m \quad (24)$$

where C_i is the concentration of chemical species "i" in solution, α_{im} is the stoichiometric coefficient of species "i" in reaction "m", and r_m is the rate of chemical reaction "m".

A set of ordinary differential equations that represented the kinetic reactions was formulated to calculate the concentration of species at different time scales. The kinetic model equations were solved using MATLAB (2019a).

3.3.3 Wet lab experiment

The kinetic model for sulfide oxidation by O_2 was tested using wet-lab experiments utilizing a batch system. Initial and final pH of the reaction solution were measured using an Orion™ pH meter. Experiments were conducted on 250 mL PW at an initial pH of 7.5 with 1 mM H_2S initial concentration spiked in the PW system. A positive pressure of air was maintained at the headspace of the flask with an air balloon to ensure that the solution was saturated with air during the experiment. The temperature of the reacting media was kept constant at 40ºC in a circulating a water bath, and the reaction solution was stirred

using a magnetic stirrer at 500 rpm. Samples were analyzed for SO_4^{2-}, $SO_3^{2-}$and $S_2O_3^{2-}$ at intervals using ion chromatography [43,44].

3.4 Results and Discussion

A potential chemical transformation pathway where O_2 and/or NO_2^- is present in a soured oil/gas/water system (see Figure 3.3) was proposed based on the literature reviewed [11]. The pathway was used to study the possible chemical transformation involving S and N species in a soured-oxic-nitrite environment in the offshore oil and gas topside separation process.

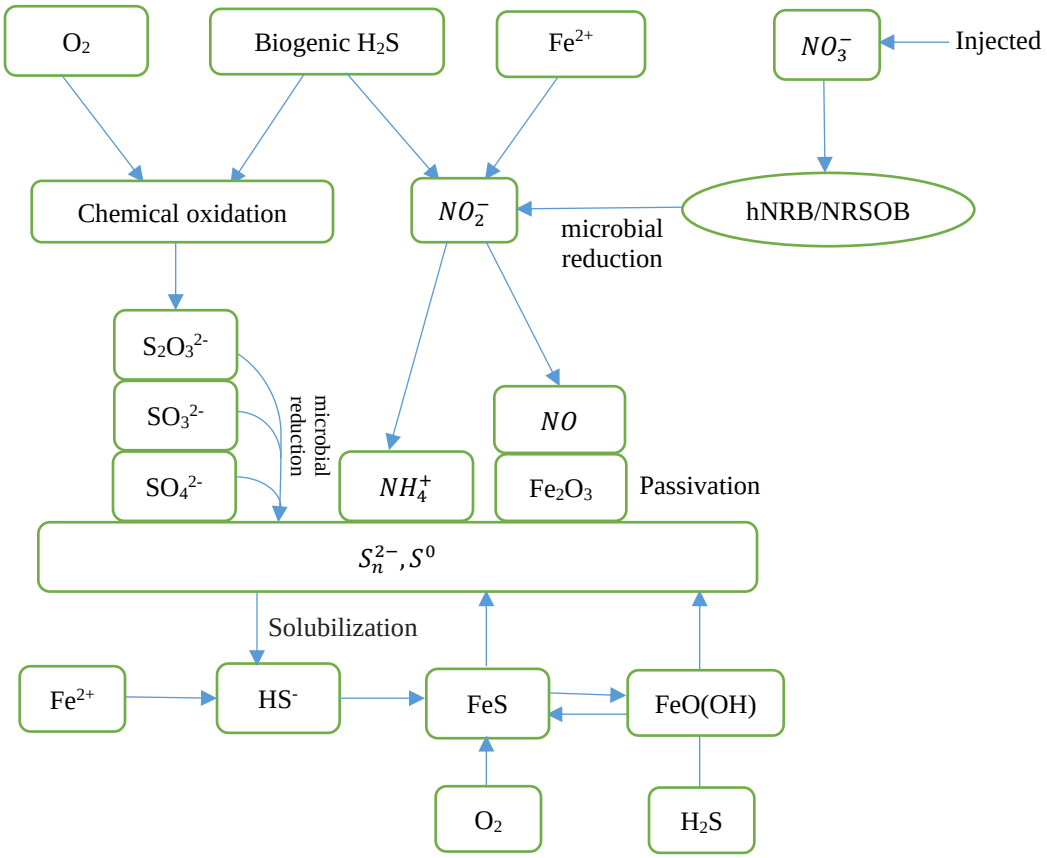

Figure 3.3: Representation of chemical transformation pathways in the sour-oxic-nitrite system

The chemical environment can greatly be influenced by O_2 and/or NO_2^- as depicted in Figure 3.3 and explained in the literature review section. Apart from various S and N species generated by sulfide reaction with O_2 and NO_2^-, FeS, $FeO(OH)$, and Fe_2O_3 were the key corrosion products formed. These compounds had significance in MIC propagation and inhibition as identified in the previous work [11].

3.4.1 Chemical equilibrium simulation

In the first part of the study, the chemical equilibrium model was used to study the composition as a function of the parameters outlined in Tables 3.2 and 3.3. Figure 3.4 shows the Modeled effect of inlet H_2S on sulfur deposition at 25°C and $1x10^5$ Pa. The model predicted S^0 and FeS generation at limited O_2 and 1 mM NO_2^-. Fe^{2+} and H_2S maintained an equilibrium state corresponding to each inlet condition. There was a high tendency of FeS formation due to the fast reaction between Fe^{2+} and H_2S [45] until an equilibrium was established. The higher the concentration of the inlet H_2S concentration, the higher the S^0 produced. At increased pressure, S^0 was formed favorably over FeS precipitation. However, FeS dominated as the temperature increases.

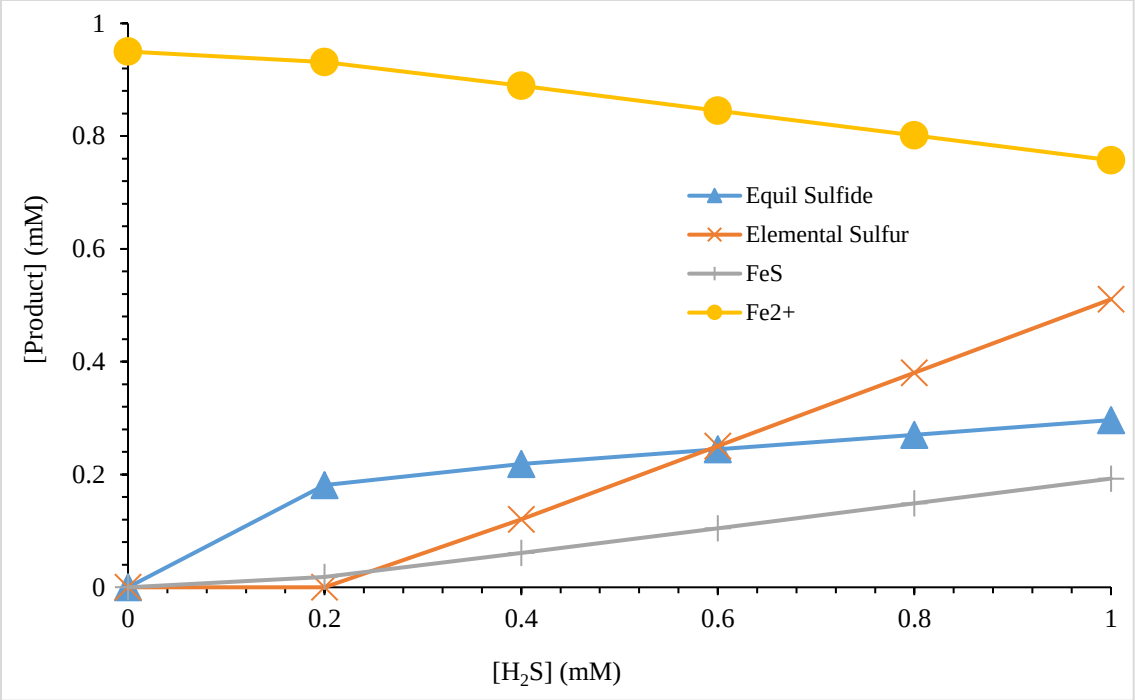

Figure 3.4: Sulfur deposition in sour system with limited oxygen and nitrite at 25°C and $1x10^5$ Pa

In a sour system saturated with O_2 and moderate levels of NO_2^- (6 mM), temperature dominated in the distribution of equilibrium products. Figure 3.5 shows the effect of temperature at atmospheric pressure. Both O_2 and NO_2^- in the system generated Fe_2O_3 and $FeO(OH)$ as a function of temperature. Fe_2O_3 was formed instead of $FeO(OH)$ at higher temperatures (95°C). This was in agreement with previous work [46]. The ΔG_f° at 298.15K of the Fe_2O_3 (-740.520 kJ/mol) and $FeO(OH)$ (-492.188 kJ/mol) could explain why Fe_2O_3 may be more thermodynamically stable and favoured. FeS was not formed at equilibrium and H_2S was completely oxidized to SO_4^{2-} at various temperatures in the system.

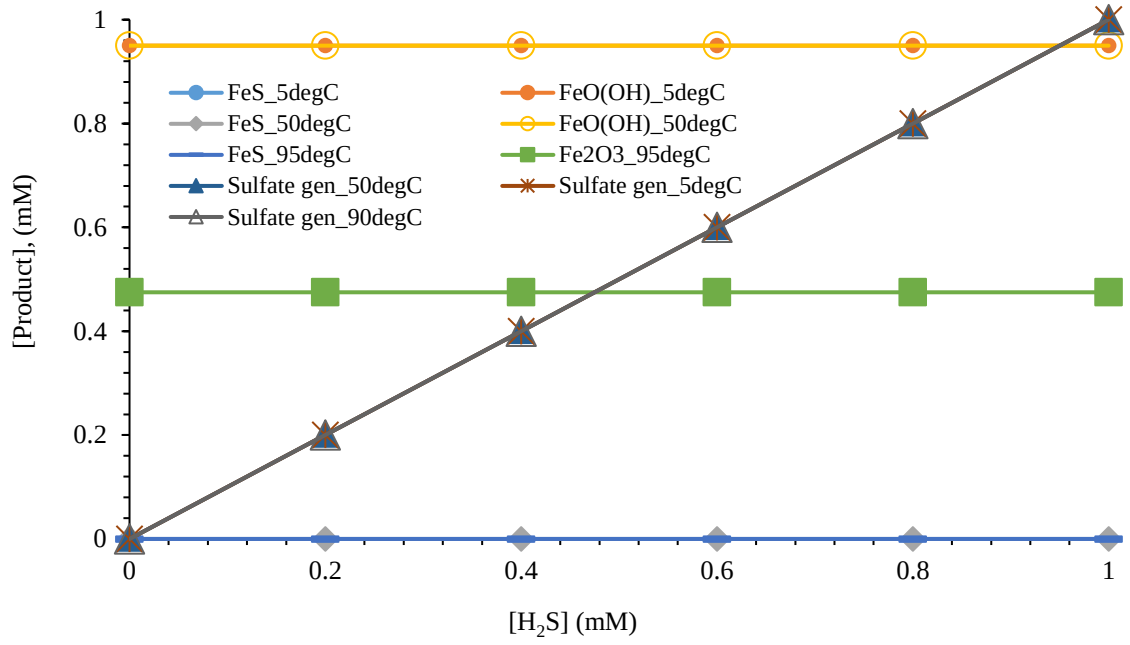

Figure 3.5: Temperature effect at $1x10^5$ Pa (H_2S_oxic_nitrite)

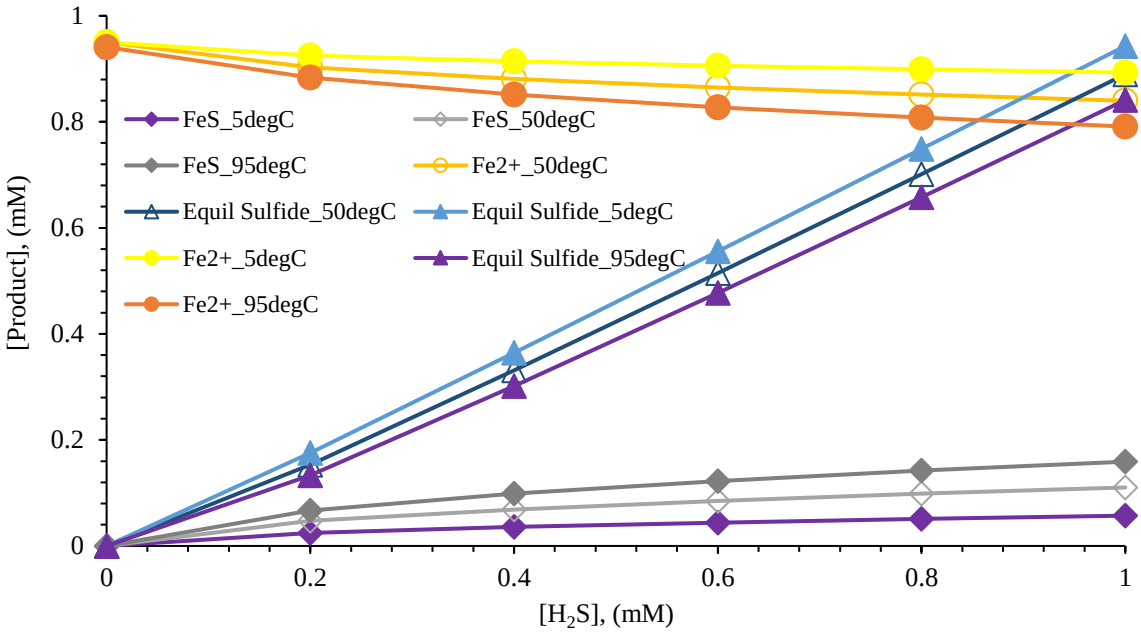

Figure 3.6: Temperature effect at $1x10^5$ Pa (H_2S_anoxic_no nitrite)

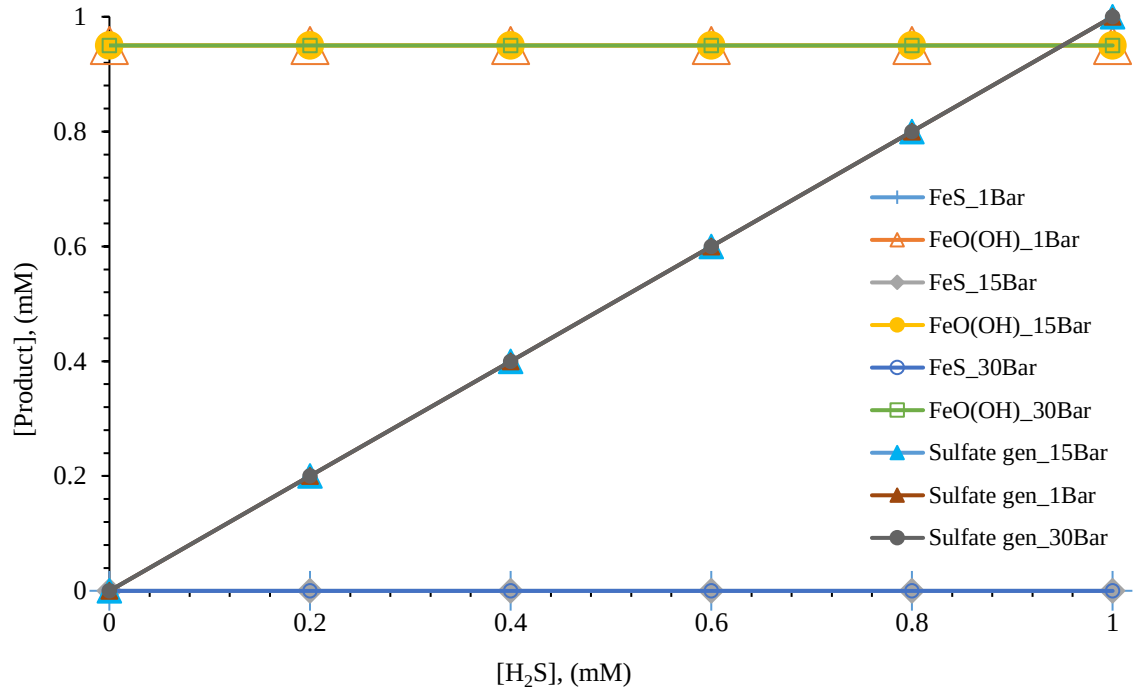

Figure 3.7: Pressure effect at 50ºC (H_2S_oxic_nitrite)

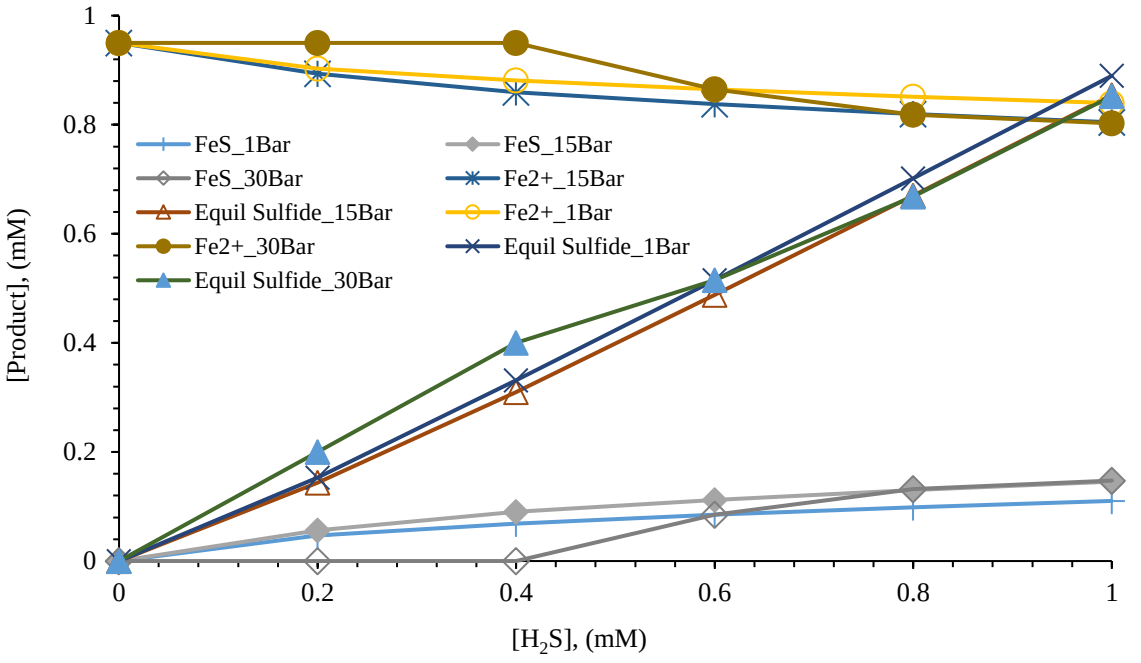

Figure 3.8: Pressure effect at 50ºC (H_2S_anoxic_no nitrite)

In Figure 3.8, the model predicted the formation of FeS at all pressures and increased with increase in the H_2S. The higher the pressure, the higher the equilibrium H_2S retained in the system.

Figures 3.9 and 3.10 show the effect of NO_2^- on sulfide system in oxic and anoxic conditions at 50ºC respectively.

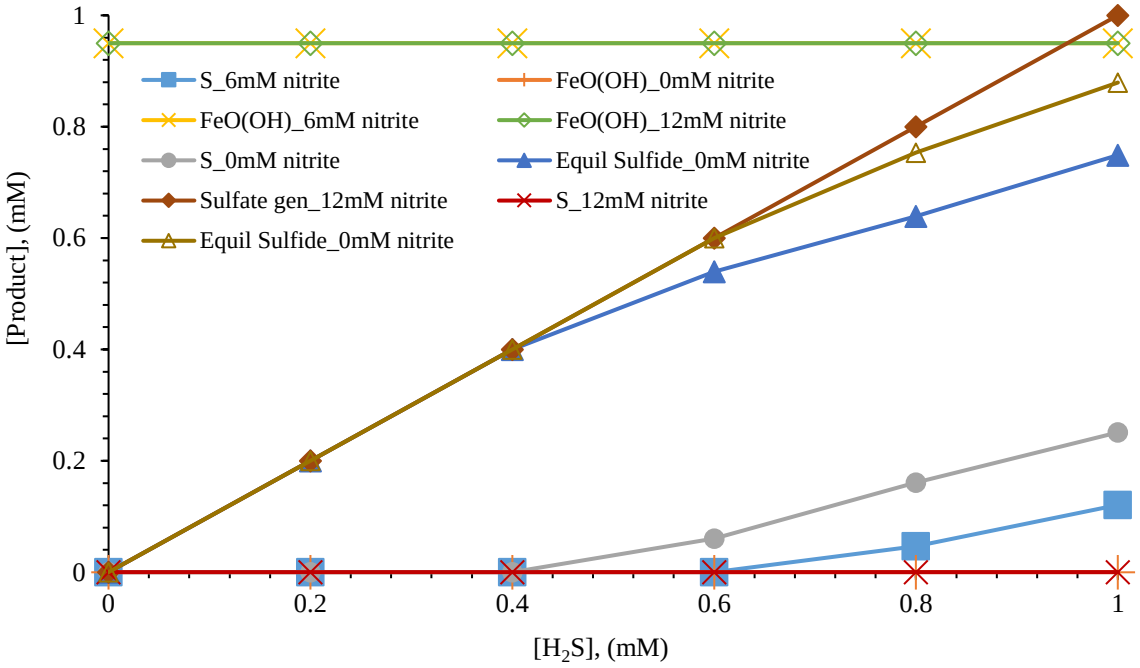

Figure 3.9: Nitrite effect at 50ºC and 1x10^5 Pa (H_2S_oxic_nitrite)

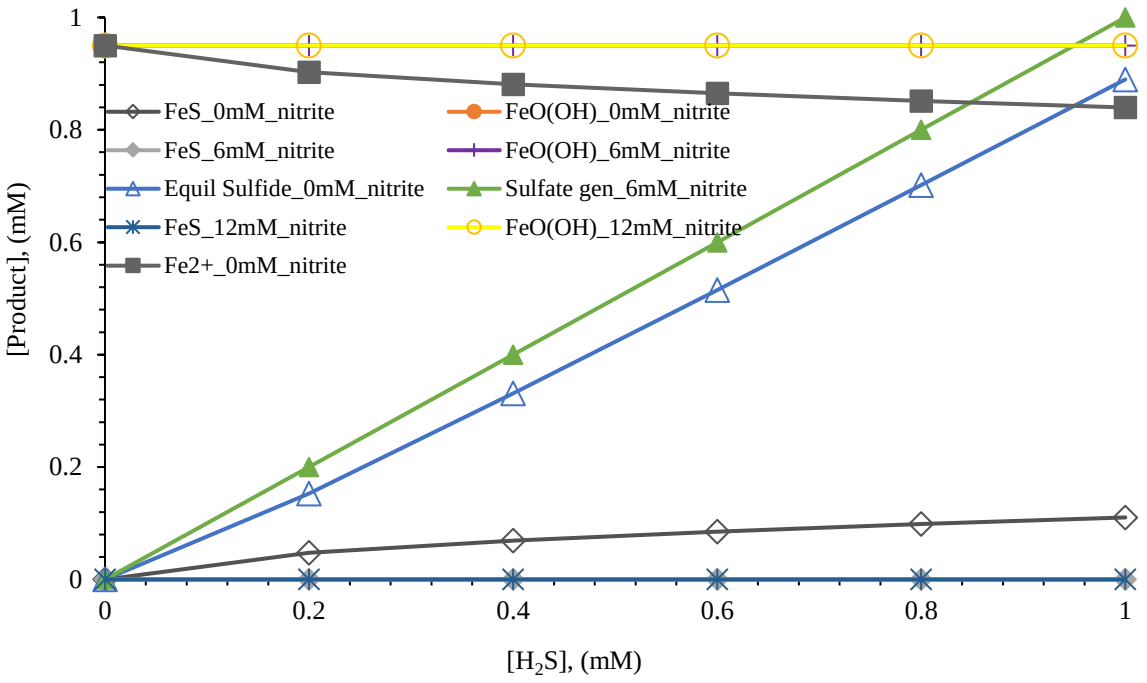

Figure 3.10: Nitrite effect at 50ºC and 1x10^5 Pa (H_2S_anoxic_nitrite)

From Figure 3.9, in the absence of NO_2^-, O_2 could partially oxidize H_2S to yield S^0 which is in equilibrium with the unreacted H_2S in the system. At higher inlet H_2S concentration, S^0 formation increased. At 6 mM NO_2^- and above, $FeO(OH)$ formation dominated over the varying H_2S inlet concentration and no sulfur formation. Figure 3.10 describes the impact of NO_2^- without O_2, a similar trend was observed in the oxic and anoxic system with respect to $FeO(OH)$. However, FeS was generated at no NO_2^- in an anoxic condition instead of S^0 while $FeO(OH)$ showed a maximum at 6 mM and 12 mM NO_2^- over the range of H_2S inlet conditions. At 6 mM NO_2^- and above, there was a high tendency of complete oxidation of H_2S to SO_4^{2-} which is the most oxidized form of S species.

3.4.2 Chemical kinetic simulation

In this part of the work, the kinetic model was used to better understand the system under time constraints. Considering a soured PW system with O_2, the kinetics of sulfide oxidation in PW was Modeled using Equations (1)-(3) and reaction rate data in seawater as described in the introduction [15]. The overall rate expressions for the production of $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-}using HS^- and O_2 precursors, are given by Equations (25)-(28) [15]. Figure 3.11 shows the kinetic model profiles.

$$d[HS^-]/dt = -k_1[HS^-][O_2]^{1.5} - k_3[HS^-][SO_3^{2-}][O_2]^{0.5} \quad (25)$$

$$d[SO_3^{2-}]/dt = k_1[HS^-][O_2]^{1.5} - k_2[SO_3^{2-}][O_2]^{0.5} - k_3[HS^-][SO_3^{2-}][O_2]^{0.5} \quad (26)$$

$$d[SO_4^{2-}]/dt = k_2[SO_3^{2-}][O_2]^{0.5} \quad (27)$$

$$d[S_2O_3^{2-}]/dt = k_3[HS^-][SO_3^{2-}][O_2]^{0.5} \quad (28)$$

where k_1 and k_3 are in $M^{-1.5}min^{-1}$, and k_2 is in $M^{-0.5}min^{-1}$, respectively.

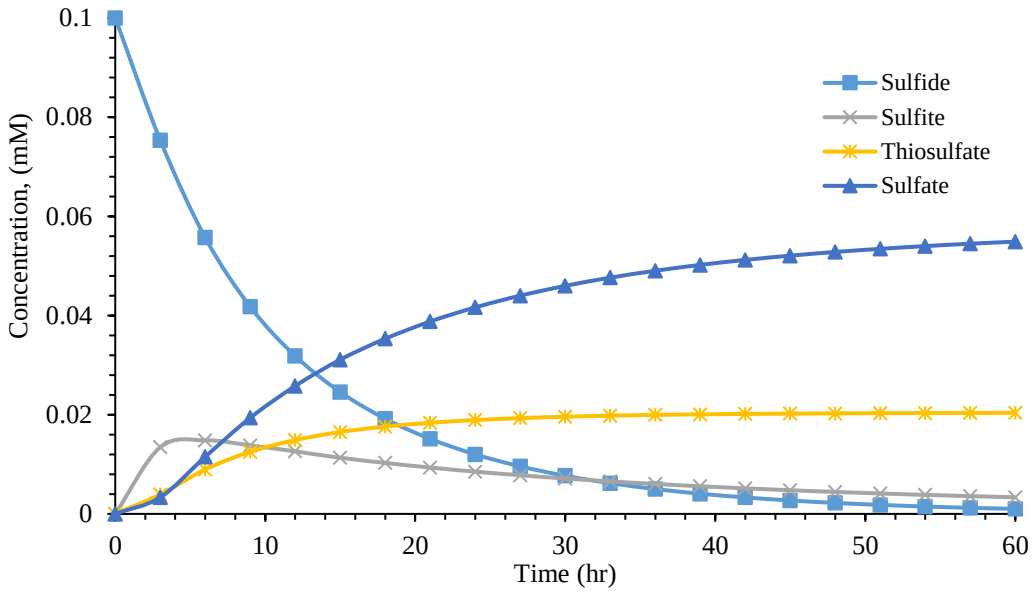

Figure 3.11: Kinetic model profile of H_2S–O_2 oxidation at 40^0C and pH 8.2

3.4.3 Kinetic model validation

The kinetic models of sulfide oxidation reactions (Equations 1-3) were validated with wet-lab experiments on field PW samples. The trends (Figure 3.12) are in agreement with the kinetic model (Figure 3.11). Hence, with this experimental outcome, the kinetic data for sulfide oxidation in seawater [15] can be adopted for PW systems under similar conditions. The deviations observed between the model predictions and experimental data can be attributed to the difference in the initial pH and buffering characteristics of the two media (seawater and PW). Pale yellow color was observed during the first 5-10 hrs of the experiment. The solution became clear and white precipitates were formed. The sulfide was oxidized partly to S^0 (white precipitate) and S_n^{2-} (pale yellow) which were not measured. This accounted for the early drop in the Total S (Figure 3.12).

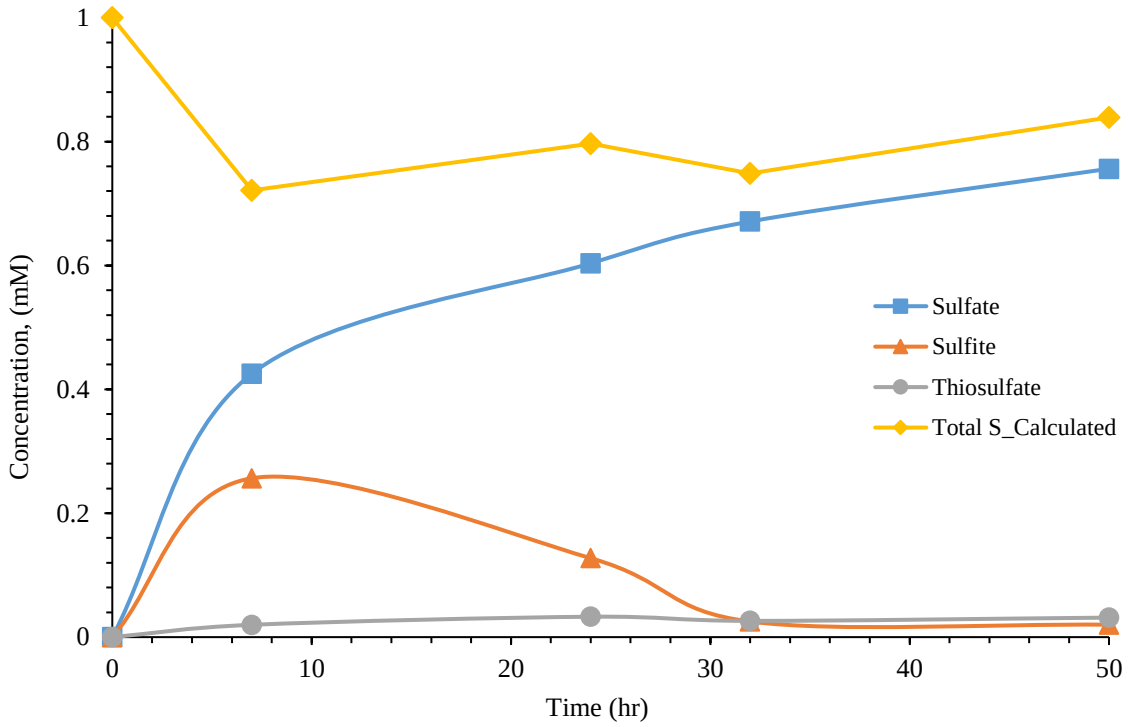

Figure 3.12: Experimental validation of H_2S–O_2 oxidation in PW at 40ºC and pH 7.5

3.5 Summary and Conclusions

In an environment dominated by SRB, the environment is soured by the biogenic H_2S produced by the SRB. The NO_2^- abiotic reaction with the H_2S is one of the mechanisms of souring control. The microbial-chemical interactions impacting MIC have complicated the understanding of the MIC mechanisms. This work investigated the behavior of the soured PW/oil system without microbial influence in response to the presence of O_2 and/or NO_2^- under different operating conditions. This is an attempt to understand the chemical system independent of microbial activity and decouple chemical-microbial relationship. It has been observed from the simulation results that the presence of sulfide, NO_2^- and/or O_2 can result in chemical transformations within the fluids due to the shift of the chemical redox

potential of the system. Such transformation may lead to the formation of corrosive species such as S^0, $SO_3^{2-}$and $S_2O_3^{2-}$, and corrosion products. These compounds impact microbial activities and are essential to the propagation or inhibition of MIC [11]. SO_3^{2-} is metastable and can reduce to produce H_2S in an acidic medium [36]. Many SRB thrive and obtain energy by reducing $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} to produce H_2S. Direct contact between S^0 and metal (or a FeS layer) can promote severe corrosion through sedimentation of S^0 or its solubilization as HS_n in a system between pH 5 and 9 [10, 29]. FeS layer is conductive and may play a key role as electron mediator between Fe^0 and S^0, therefore, accelerate corrosion rates to as high as >20 mm/y [29]. The conductive FeS and $Fe(OH)_3$ deposits serve in electron transport during iron reduction by IRB and electron acceptor for microbial activities respectively [49,50]. Passivating Fe_2O_3 layer acts as an anodic corrosion inhibitor by preventing further dissolution of Fe^0 as Fe^{2+} [35].

It was observed experimentally, and through modeling, that sulfide can be oxidized chemically via O_2 or NO_2^-. The implication for a soured chemical environment is the formation of corrosive species and the impact on microbial activities (growth/inhibition). NO_3^- is used to mitigate reservoir souring and is often reduced to NO_2^- by NRB or soNRB activities. The impact of NO_2^- on corrosion downstream is not well understood. The simulation and preliminary experimental outcomes confirmed that NO_2^- may react chemically with sulfide. Due to its reactivity, sulfide can be rapidly cosumed chemically alongside microbial pathways [2], which requires continued investigation. The following are the main conclusions drawn from the current studies:

- The equilibrium model provided a better understanding of the chemical transformation of species in sulfide-oxic-nitrite environment in the offshore oil and gas topside separation process.
- FeS, $FeO(OH)$, and Fe_2O_3 were the key corrosion products predicted by the equilibrium model. These compounds agree with the chemical transformation pathways described in the literature.
- Low nitrite concentration (0.2–1 mM) favored the formation of S^0 over SO_4^{2-} as the inlet H_2S concentration increased while FeS dominated with increase in temperature.
- In presence of nitrite, $FeO(OH)$ was formed, which transformed to a more stable and passivating Fe_2O_3 at elevated temperatures above 50°C. Therefore, souring control by NO_2^- should be in a range where SRBs are inhibited but not so high as to cause chemically driven nitrite corrosion. Based on this work a potential range is 150-500 mg/L.
- The modeling approaches demonstrated in this work can serve as tools to better understand the chemistry of S and N species in the offshore oil and gas topside separation process and indication of the contributory effect of chemical transformation on the overall corrosion.
- This study will inform further work in the integration of chemical, microbial and risk models for a better MIC management strategies for offshore oil and gas platforms. For example, the effect of the changing operating conditions (temperature, pressure and composition) on sulfide, NO_2^-, and corrosion products

(FeS, FeO(OH), and Fe_2O_3) described in this study can be used to identify the potential corrosion in the production facilties based on pressure, temperature, and composition of the fluids.

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4 EXPERIMENTAL INVESTIGATION OF SULFIDE–NITRITE CHEMICAL REACTION IN PRODUCED WATER SYSTEM

Preface

A version of this manuscript has been submitted in the Canadian Journal of Chemical Engineering. I am the primary author of this work. Along with me are the co-authors; Reza Akhoondi, Mahsan Basafa, Kelly Hawboldt, Christina Bottaro and Faisal Khan. I conceptualized the idea, conducted the literature review. I carried out the experimental design, setup, analysis, and interpretation of data. I prepared the original draft of the manuscript and subsequently revised the manuscript based on the co-authors' feedback. The co-authors Reza Akhoondi and Mahsan Basafa assisted in experimental design and setup, analytical method development and chemical analysis. Kelly Hawboldt supervised the work, helped in the concept development, reviewed, and edited the manuscript. Christina Bottaro helped to design the experiment, advised on analytical methods, prepared, and edited the manuscript. Faisal Khan contributed to preparing, reviewing, and editing the manuscript.

Publication:

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Abstract

Seawater is used to enhance oil recovery on offshore platforms, however, it can also result in reservoir souring. Nitrate injection has been used to control souring by the promotion of growth of nitrate-reducing bacteria (NRB) which out-compete sulfate-reducing bacteria (SRB) for nutrients. Treatment can reduce sulfide production and improve safety and operational issues associated with sulfide, including microbiologically influenced corrosion (MIC). However, little is known about the chemical reactions between sulfur and nitrogen compounds in these systems and the potential impact on corrosion. For example, nitrate is stable in water, soured produced water (PW), or seawater; it is rapidly reduced to nitrite by NRB suggesting that nitrite is the reactive species in treatment rather than nitrate. In this work, we investigated the reactivity of nitrite with sulfide under a range of conditions. Experiments indicate sulfides in these media are oxidized by nitrite to yield polysulfide, elemental sulfur, and ammonium under weakly acidic to weakly basic conditions. However, sulfide forms the insoluble iron sulfide in the presence of iron (II) in PW, which removes the sulfide from the oxidative transformation pathway. The rate of consumption of sulfide was pseudo-first-order with a rate constant of $0.4369\ \mathrm{h}^{-1}$ in seawater with a large excess of nitrite at 45ºC, and pH 7.6. In experiments with distilled water (pH 7.2), the rate of sulfide oxidation increases with nitrite concentration reaching similar rates as to those in seawater. More than 97% of the initial sulfides were consumed in 7 h in all cases. The results of this study provide a better understanding of the chemistry of sulfide and nitrite transformation in PW, seawater, and water systems. The data provides

insight into the importance of the reaction of nitrite and sulfide and must be considered in MIC management outside the microbial inhibition of sulfide formation.

Keywords: Chemical reaction, wet-lab experiment, produced water, kinetics, microbiologically influenced corrosion (MIC)

4.1 Introduction

The formation of biogenic hydrogen sulfide in oil and gas reservoirs poses risks to human health and the integrity of oil-extraction assets [1,2]. Microbial sulfate reduction (MSR) is the prime source of the biogenic sulfide in the reservoir particularly under anaerobic conditions [3]. Souring and corrosion issues can be more severe if produced water (PW) is reinjected into the reservoir due to the presence of organic compounds as carbon sources (e.g., acetate) [4–6]. The conventional method of treating soured systems is the introduction of various oxidizing agents including sodium hypochlorite, hydrogen peroxide, and potassium permanganate, etc., which convert hydrogen sulfide to less hazardous sulfur compounds. However, there are limitations and drawbacks associated with each method [7]. Souring is mostly controlled in the reservoir and topside infrastructure by the application of nitrate and biocides respectively [8,9]. Biocides are organic chemicals designed to kill a broad range of microorganisms. The choices of the biocide type and optimal strategy of application are determined by the possible toxicity of biocides in the environment and the cost implications of the biocide use [10]. Nitrate is relatively nontoxic, has a high solubility in water, and compatibility with other chemicals making it an attractive option [9].

The application of nitrate (NO_3^-)/nitrite (NO_2^-) is considered a promising souring mitigation approach, and subsequent MIC control during seawater injection or PW reinjection (PWRI) [11,12]. There are different mechanisms by which NO_3^- controls souring or corrosion depending on the environmental/chemical conditions (see Figure 4.1).

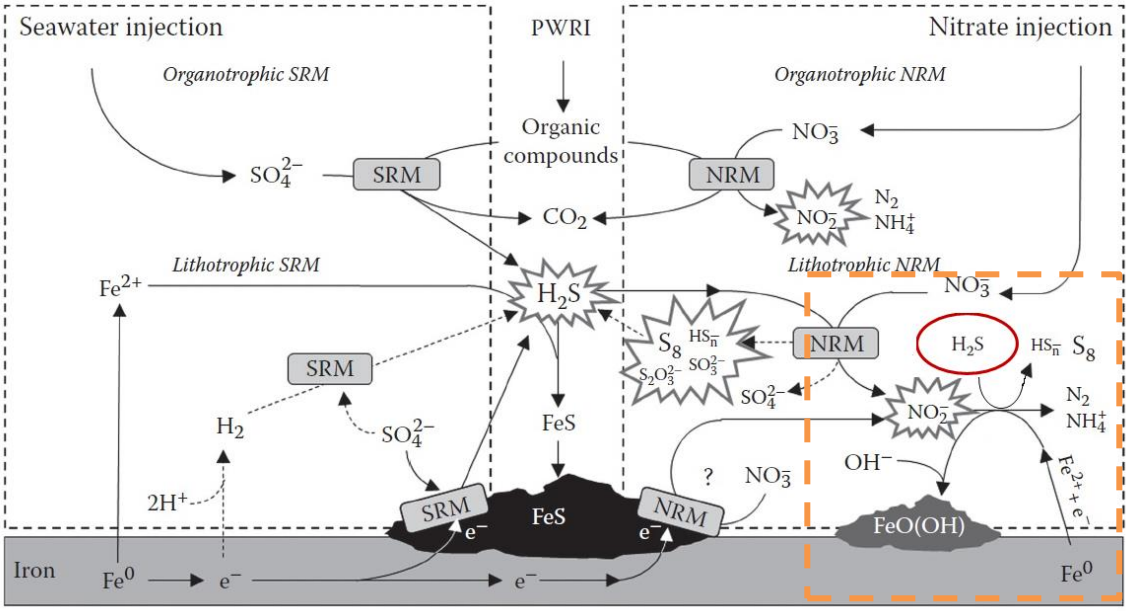


Figure 4.1: Microbial/chemical processes during seawater injection, produced water reinjection, and nitrate injection at oilfield production operations, adapted from Lahme et al [13] with modification

NO_3^- is an energetically more favorable electron acceptor than SO_4^{2-} and stimulates the activities of heterotrophic bacteria to outcompete sulfate reducers for electron donors such as organics (also known as bio-competitive exclusion). NO_3^- is reduced to NO_2^- by the nitrate-reducers, which inhibits sulfate reducers' activities and suppresses souring. Also, sulfide-oxidizing nitrate reducers can utilize sulfide produced by the sulfate reducers as an electron donor to produce toxic nitrite [11,13,14]. Another important mechanism of sulfide removal is the chemical reaction of NO_2^- with sulfide to produce polysulfide (S_n^{2-}) and subsequently, precipitate into elemental sulfur (S^0). Equations 1 and 2 are examples of the reactions, but other stoichiometries are possible depending on the S_n chain length [15,16]. However, the chemical reactions of NO_3^- with HS^- is kinetically unfavorable [17].

$$4HS^- + NO_2^- + 5H^+ \rightarrow HS - S - S - S^- + NH_4^+ + 2H_2O \quad (1)$$

$$HS - (S)_7 - S^- \rightarrow S_8 \downarrow + HS^- \quad (2)$$

It has also been reported that NO_2^- may react with Fe^{2+} in sour systems to form an oxide of Fe^{3+} such as Fe_2O_3 and $FeO(OH)$, which inhibits further corrosion at the surface of mild steel (Equation 3) [18]. This reaction does not proceed at a pH below neutral. The protective Fe oxide layer becomes unstable at pH <6 and the corrosion rate increases [12,18].

$$2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow 2NO + Fe_2O_3 + H_2O \quad (3)$$

In sour PW system, Fe^{2+} interferes with the kinetics of NO_2^- chemical reaction with sulfide. Fe^{2+} spontaneously reacts with hydrogen sulfide and precipitates as iron sulfide (FeS) (Equation 4) [19–21]. The formation of the FeS precipitates further complicates the understanding of the hydrogen sulfide oxidation via NO_2^-.

$$Fe^{2+} + HS^- \longleftrightarrow FeS + H^+ \quad (4)$$

The chemistry of the local environment can have growth or inhibitory impacts on microbial activities leading to MIC [22]. For instance, reactive species that are produced or consumed in microbially mediated reactions may also undergo chemical transformations as in the case of NO_2^-. The synergistic effect may lead to the competitive contribution of promoting or inhibiting MIC. It is, therefore, imperative to understand the chemistry of the system in isolation from microbially driven reactions. Little is known about the reactivity and kinetics of sulfide and NO_2^- in produced water systems, which account for the data gaps. The bulk

of published work [14–16,23] focused on microbially-driven transformations of sulfide and nitrite and/or nitrate in oil and gas systems without considering the contribution of the chemical reactions.

An experimental investigation of the chemical transformation of S and N species in the PW, seawater, and water system was conducted as demonstrated above, these species play a key role in MIC. The experiment involved the anoxic reaction of sulfide (0.03 M initial concentration) and NO_2^- (0.07 M initial concentration) in PW, seawater, and water at 45ºC and initial pH of 7.2-7.6. However, in this work, we attempted to decouple the chemistry from microbial activities to better understand the interactions. As such the microbial impacts were not considered. The understanding of the rate of these reactions will inform microbial studies in MIC management.

The first section of the paper introduces the background and relevance of sulfide-nitrite chemical transformation in the soured environment and highlights the problem statement, objective, and the limitation of the study. The second section presents the details of the chemicals, a description of the experimental setup, and the analytical methods used. The third section discusses the outcomes of the experimental investigation and presents the data generated. The fourth section summarizes the outcome of the study, highlights the major conclusions, and recommendations.

4.2 Materials and methods

4.2.1 Chemicals

Certified grade hydrogen sulfide water (0.4 wt% H_2S) and crystalline potassium nitrite (KNO_2, ≥96%) were purchased from Fisher Scientific (Ottawa, ON, Canada). The chemicals were the precursors for the investigation of sulfide oxidation via NO_2^- and were used as received without any pretreatment. The seawater and produced water samples were collected from the SeaRose offshore platform, NL, Canada. The samples were stored at 4°C before the experiment. Deionized water was used for all experimental procedures.

4.2.2 Experimental Setup

A batch system was used for the experiments of sulfide oxidation by nitrite as illustrated in Figure 4.2. All reactions were carried out in a 250 mL 3-neck round bottom flask fitted with an inlet for flushing the system with nitrogen and degassing and outlet to purge the system with nitrogen to maintain anoxic conditions as needed. At the beginning of each experiment, the dissolved oxygen was removed from the solution by a sequence of sparging with nitrogen and degassing under vacuum for 60 minutes and maintaining minimum headspace throughout the experimental period to operate as close to anoxic solution conditions as possible. It was ensured that all joints and lids were tight, and nitrogen was reinjected before the experiment. This procedure ensures that the O_2 was limited in the solution to cause an unwanted reaction between O_2 and sulfide. The temperature of the reacting media was kept at 45ºC using a water bath, and the reaction solution was stirred

using a magnetic stirrer at 500 rpm. The initial pH of the solution media was not adjusted, and the solution was not buffered. Initial and final pH of the reaction solutions were measured using an Orion™ pH meter (Fisher Scientific, Mississauga, ON, Canada).

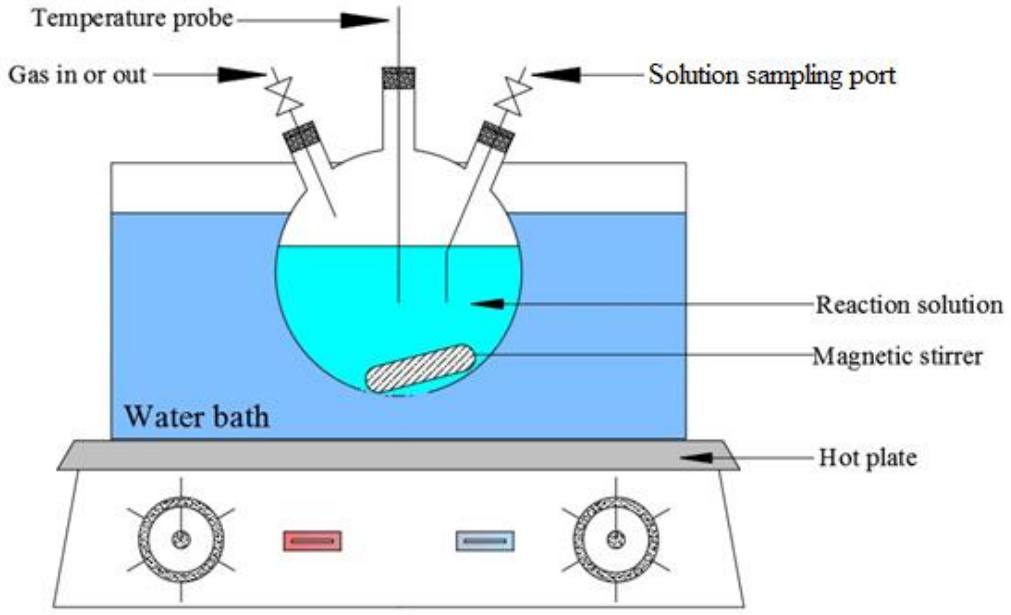


Figure 4.2: Experimental setup used for the experiments of sulfide oxidation by NO_2^-

Experiments were conducted in three different types of water of varying complexities (see Table 4.1); Case 1: addressing the impact of NO_2^- in soured PW at an initial pH of 7.5; Case 2: studying the sulfide–NO_2^- reaction rate in seawater at an initial pH of 7.6; and Case 3: studying the behavior of NO_2^- in soured water at an initial pH of 7.2.

Table 4.1: Summary of the experimental cases presented in this work.

	Experimental study (No oxygen)	Temperature (ºC)	Initial pH	Initial concentration (M)	
				Sulfide	Nitrite
Case 1	Sulfide-NO_2^- reaction in PW	45	7.5	0.03	0.07
Case 2	Sulfide-NO_2^- reaction in seawater	45	7.6	0.03	0.07
Case 3	Sulfide-NO_2^- reaction in water	45	7.2	0.03	0.07
Case 4	Sulfide-NO_2^- reaction in water	45	6.5	0.014	0.07, 0.028, 0.014

Initial concentrations of H_2S and NO_2^- were 0.03 M and 0.07 M, respectively, in PW and seawater, and water. The concentrations were chosen based on the range of sulfide present in soured reservoir fluids and NO_2^- concentrations are sufficient to oxidize the sulfide in the solution according to previous studies [7,13,23,24]. The samples were taken for analysis at 1 h intervals for 7 h. HS^-/NO_2^- reaction occurs between 25ºC and 70ºC and circumneutral pH [7,25].

For case 1, the experiment was set up to verify the impact of NO_2^- in soured PW at an initial pH of 7.5 and anoxic condition. The reaction temperature was maintained at 45ºC and monitored for 7 h. For case 2, the experiment was conducted to determine the rate of sulfide disappearance in the presence of NO_2^- in seawater at an initial pH of 7.6 and in anoxic condition. The reaction temperature was maintained at 45ºC and monitored for 7 h. Similarly, experimental case 3 was to study the behavior of NO_2^- in soured water at an initial pH of 7.2 and the reaction temperature was maintained at 45ºC. The reaction was

monitored for 7 h. For case 4, the experiment was conducted to investigate the behavior of NO_2^- in soured water at an initial pH of 6.5 and varying NO_2^- concentrations. The reaction temperature was maintained at 45ºC and monitored for atleast 7 h.

In experimental case 2, the rate of sulfide consumption in Equation 1 was modeled using a batch system rate expression (Equations 5 and 6) with the following assumptions.

- The system volume is constant (liquid-phase reactions) and well stirred.
- The concentration of NO_2^- remains constant. The NO_2^- concentration is in great excess of sulfide and much more than the stoichiometric requirement as in Equation 1.
- The reaction is a pseudo-first-order reaction with respect to sulfide.

$$-r_{HS^-} = \frac{d[HS^-]}{dt} = k[HS^-]^n[NO_2^-]^m \quad (5)$$

If the nitrite concentration is in large stoichiometric excess, then

$$-r'_{HS^-} = \frac{d[HS^-]}{dt} = k'[HS^-]^n \quad (6)$$

Where $k' = k[NO_2^-]^m$

4.2.3 Analytical methods

Aqueous samples were analyzed for NO_2^- and SO_4^{2-} using an ion chromatograph (Dionex, DX-120) equipped with a Dionex ASRS-ULTRA 4 mm ion suppressor (Dionex Corporation, CA, USA) and fitted with an IonPac AS-22 (4 x 250 mm) HPLC ion-exchange column mounted in a column oven and held at 30 ºC. The mobile phase was

deionized water 3.0 mM in Na_2CO_3 and 2.5 mM in $NaHCO_3$ at a flow rate of 1.5 mL/min flow rate. The reaction was followed by removing 3 mL of the sample solution through the sampling port; this aliquot was filtered using a 0.45 mm membrane filter to remove suspended solids before analysis. Total sulfide and ammonium (NH_4^+) concentrations in the water samples were determined spectrophotometrically using the methylene blue method [26] at 670 nm wavelength and the indophenol method [27,28] at 630 nm wavelength respectively.

4.3 Results and discussion

4.3.1 Experimental Case 1: Impact of NO_2^- in Soured PW

The PW solution in Run 1 contained only sulfide and Run 2 contained both sulfide and NO_2^- as described in Table 4.2.

Table 4.2: Experimental Runs to Assess the Impact of NO_2^- in Soured PW–Experimental Case 1

Run	Reaction Solution	Temperature (ºC)	Initial pH	Initial concentration
Run 1	PW + H_2S	45	7.5	H_2S: 0.03M
Run 2	PW +H_2S + NO_2^-	45	7.5	H_2S: 0.03M and NO_2^-: 0.07M

In all experiments in Case 1, the solution turned black after the addition of sulfide due to the precipitation of $FeS_{(S)}$ (Equation 4). This observation was in agreement with previous work indicating the rapid precipitation of HS^- by Fe^{2+} in the system [20,29]. After 1-2 h,

the black coloration in Run 2 gradually disappeared. As NO_2^- was consuming HS^- in the system, the reaction caused more FeS dissolution in the reverse reaction by shifting the equilibrium to favor the formation of soluble Fe^{2+} and HS^-.

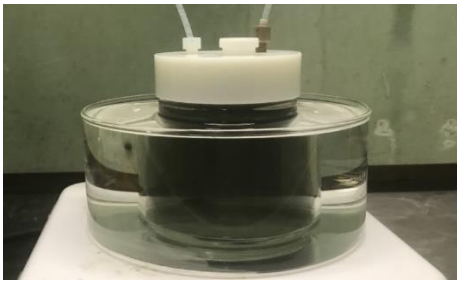
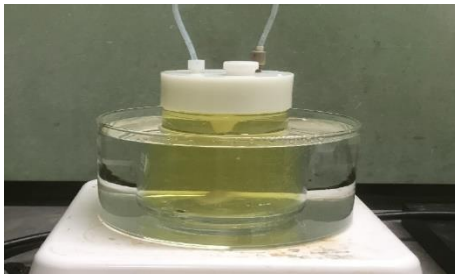
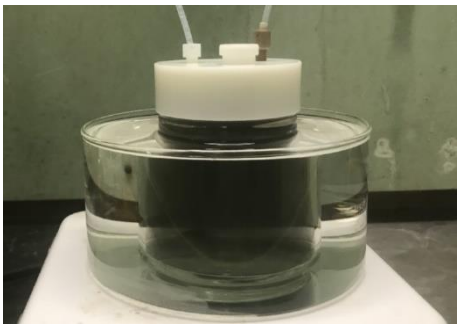
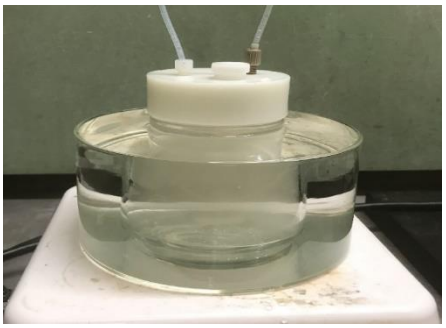
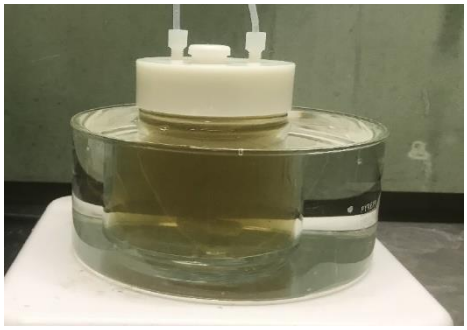
Observation Time	**Run 1: PW spiked with H_2S**	**Run 2: Treated PW spiked with H_2S**
At 4 h	 A. FeS precipitates (black)	 D. Yellow solution indicating polysulfide formation
At 7 h	 B. Unchanged from A	 E. Clear solution with whitish elemental S^0 precipitate
At 9 h	 C. NO_2^- was added at 7 h, yellow-grey solution indicating polysulfide formation with some FeS remaining after 2 h of NO_2^- addition	

Figure 4.3: Observation of $NO_2^- - HS^-$ chemical transformation in PW with time

At 4 h, the reaction solution in Run 2 turned yellow due to the formation of polysulfide (Figure 4.3D). The yellow coloration in Run 2 gradually disappeared and the solution became clear with a white precipitate of S^0 as shown in Figure 4.3E. Polysulfides with different chain lengths '*n'* and elemental sulfur was formed (Eqs. 1 and 2) [15,16].

Meanwhile, the Run 1 remained the same with black FeS precipitate (Figure 4.3A and B) until 7 h, which we propose can be attributed to the chemical equilibrium of HS^-/Fe^{2+} reaction (Equation 4). At 7hrs, the Run 1 solution setup was spiked with NO_2^- to observe the effect on the sulfide-containing system. A yellowish color was observed after 2 h of NO_2^- addition, indicating reaction progress (Equation 1) and the formation of polysulfides (Figure 4.3C). A rust-brown gelatinous precipitate was also observed settling at the bottom of the flask in Run 2. The precipitate may be a form of insoluble Fe(III) oxide [30], as described in Equation 3.

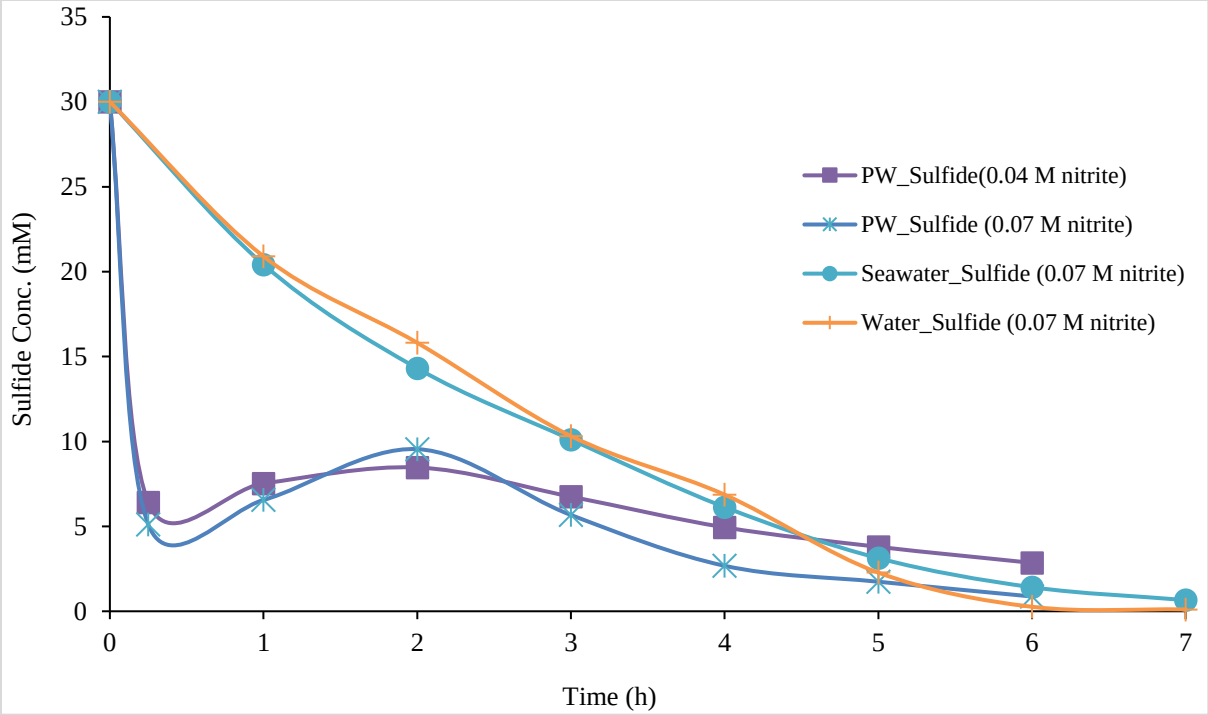


Figure 4.4: Sulfide consumption rate by NO_2^- in PW (0.07 and 0.04 M NO_2^-), seawater and water at pH 7.5, 7.6 and 7.2 respectively

An attempt was made to study the behavior of sulfide consumption by NO_2^- in PW at 0.04 M and 0.07 M NO_2^-concentrations (Experimental Case 1). Figure 4.4 shows the rate of sulfide consumption by NO_2^- in PW, seawater, and water. The trend of the sulfide consumption in PW differs from the pathways in seawater and water, which can be attributed to the Fe^{2+} impact in PW. The rapid precipitation reaction (Equation 4) between Fe^{2+} and HS^- to form FeS is likely the cause of the sharp drop in sulfide concentration (Figure 4.4). Sulfide concentration then slightly increases until it reaches equilibrium at 2 h and then flattens out. The pattern suggests the kinetic-equilibrium state in the system involving FeS. The process of FeS precipitation in Equation 4 can be interpreted in terms of two competing reactions (Equations 7 and 8) according to [20].

$$Fe^{2+} + 2HS^{-} \longrightarrow Fe(HS)_{2(s)} \quad (7)$$

$$Fe(HS)_{2(s)} \longrightarrow FeS_{(s)} + H_2S \quad (8)$$

The first stage involves the rapid consumption of HS^- by Fe^{2+} as described in Equation 7 while the second stage of the reaction involves the transformation of $Fe(HS)_2$ to FeS with the release of H_2S back into the solution (Equation 8). This explains the slight increase in the sulfide concentration after its sharp drop as shown in Figure 4.4. The final pH of the solution was 8.5. The increase in the pH can be attributed to the generation of NH_4^+ as a product of the reaction. A study in [7], suggests that a portion of the product S^0 and ammonia (NH_3) products may revert to HS^- through a S_n^{2-} stage, especially at a pH above 9. Such a reverse reaction may decrease the consumption of HS^-.

It should be noted that NO_2^- partially consumes HS^- in the solution at the beginning of the experiment. However, as time progresses, distinguishing between competing reactions (NO_2^-/HS^- and Fe^{2+}/HS^-) becomes difficult. This interference complicates the interpretation of HS^-/NO_2^- reaction kinetics in the PW system.

4.3.2 Experimental Case 2: Kinetic Study of Sulfide Consumption by NO_2^- in Seawater

Due to the competing consumption of HS^- by Fe^{2+} and NO_2^- in the PW system, the rate of HS^-/NO_2^- reaction in seawater was investigated where there was no or negligible Fe^{2+} present. The change in the concentration of the sulfide was examined as a function of time

at a single initial sulfide concentration. Figure 4.5 shows the plot of sulfide concentration in seawater at an initial pH 7.6, which originally contained 0.03 M sulfide.

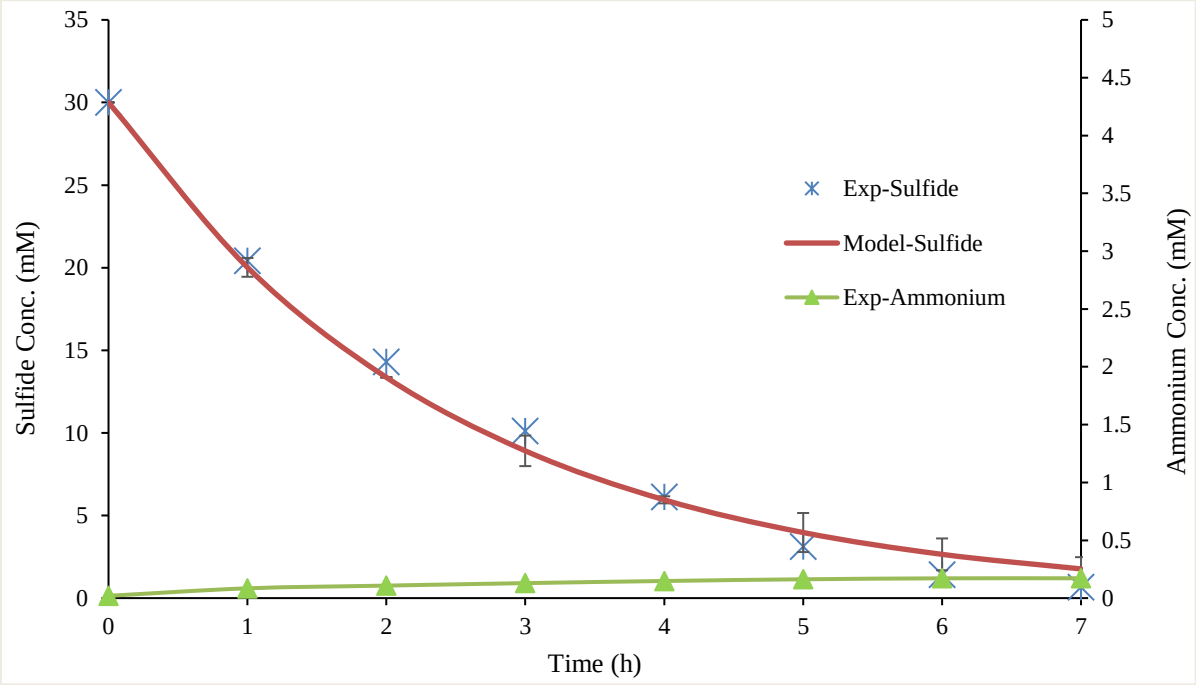


Figure 4.5: Sulfide consumption by NO_2^- and ammonium production in seawater at initial pH 7.6

In this study, the NO_2^- concentration was in large stoichiometric excess of sulfide and did not decline measurably during the course of the experiment despite the substantial declines in the sulfide concentrations. Under these conditions, the consumption reaction obeys pseudo-first-order kinetics and leads to the production of ammonium. The experimental results are in good agreement with the work of Frost J and Snyder K [7], more than 97% of the initial sulfide were consumed after 7 h. The integrated rate law was used to determine the rate constant and reaction order for the disappearance of sulfide, as shown in Figure

4.6. The plot is consistent with the behavior of a system that obeys a pseudo-first-order rate law with a rate constant, $k = 0.437\ h^{-1}$.

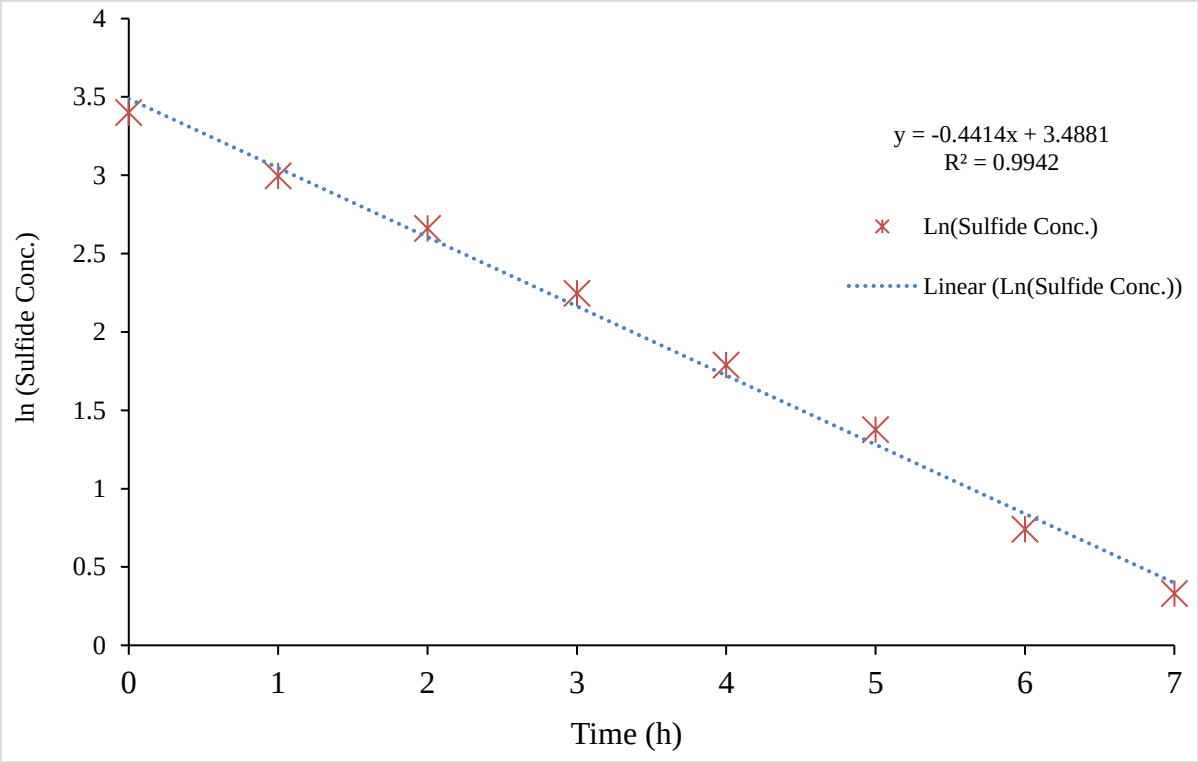


Figure 4.6: Order of sulfide consumption rate by NO_2^- in seawater at initial pH 7.6

4.3.3 Experimental Case 3: Behavior of NO_2^- in Soured Water at initial pH 7.2

The PW and seawater may exhibit buffering capacity due to the presence of bicarbonate and carbonate ions. PW and seawater can resist drastic pH changes even after the addition of weak bases and acids. Such a phenomenon may impact the sulfide oxidation with nitrite. This experiment was conducted to study the impact of NO_2^- in soured water with a low tendency of buffering at an initial pH of 7.2 and 45ºC. Figure 4.7 shows the rate of sulfide

consumption in the water at pH 7.2, which originally contained 0.03 M sulfide and 0.07 M NO_2^-.

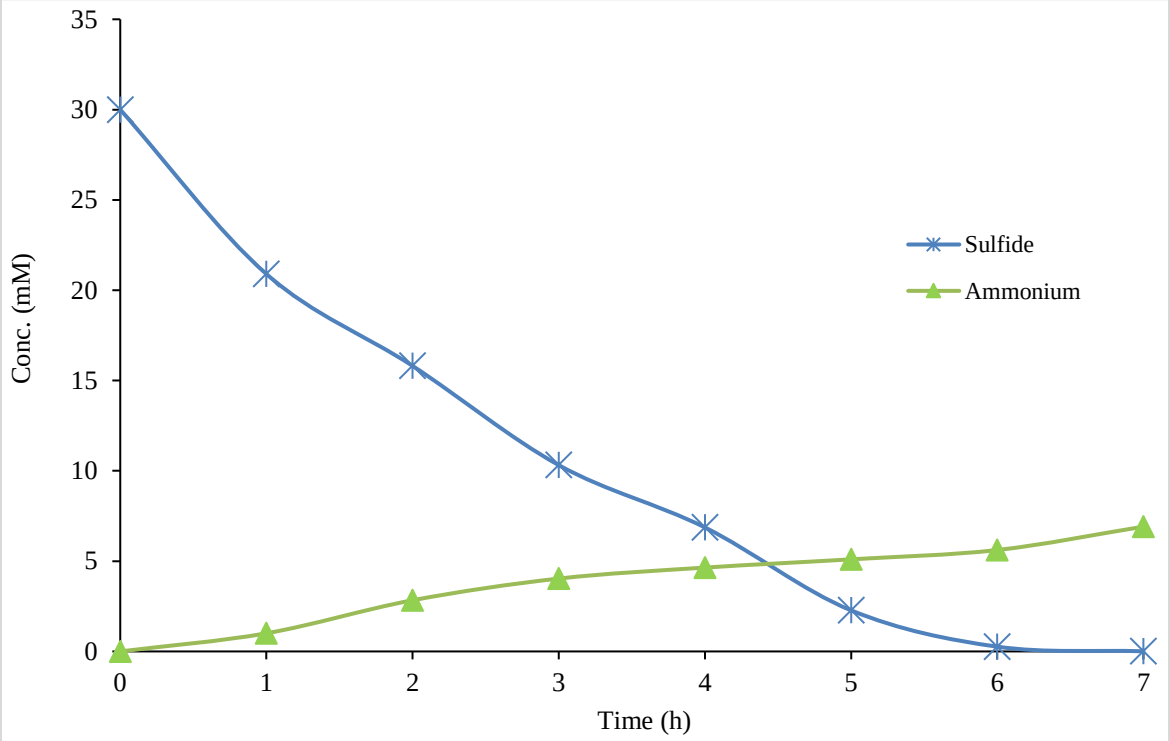


Figure 4.7: Sulfide consumption rate by NO_2^- in water at initial pH 7.2

The result showed that the sulfide-NO_2^- reaction progressed quite well at about neutral pH (Figure 4.7). More than 99% of the initial sulfide was consumed after 7 h. The sulfide concentration decreased smoothly with time and follow a similar trend as in seawater. However, NH_4^+ was generated measurably than in seawater under the same conditions. It is worthwhile to note that the initial pH and solution buffer can impact the sulfide speciation and consumption in the solution.

4.3.4 Experimental Case 4: Behavior of NO_2^- in Soured Water at initial pH 6.5

The experimental cases 1-3 investigated the sulfide-NO_2^- reaction at the original pH of the reaction media. Experimental case 4 intended to simulate the potentially lower pH of samples under pressurized systems. This experiment was conducted to study the behaviour of varrying NO_2^- concentration in soured water at an initial pH of 6.5 and 45ºC. The initial solution pH was adjusted with CO_2 to achieve the desired pH. Figure 4.8 shows the rate of sulfide consumption in the water at initial pH 6.5, which originally contained 0.014 M sulfide and 0.07, 0.028, 0.014 M NO_2^- respectively.

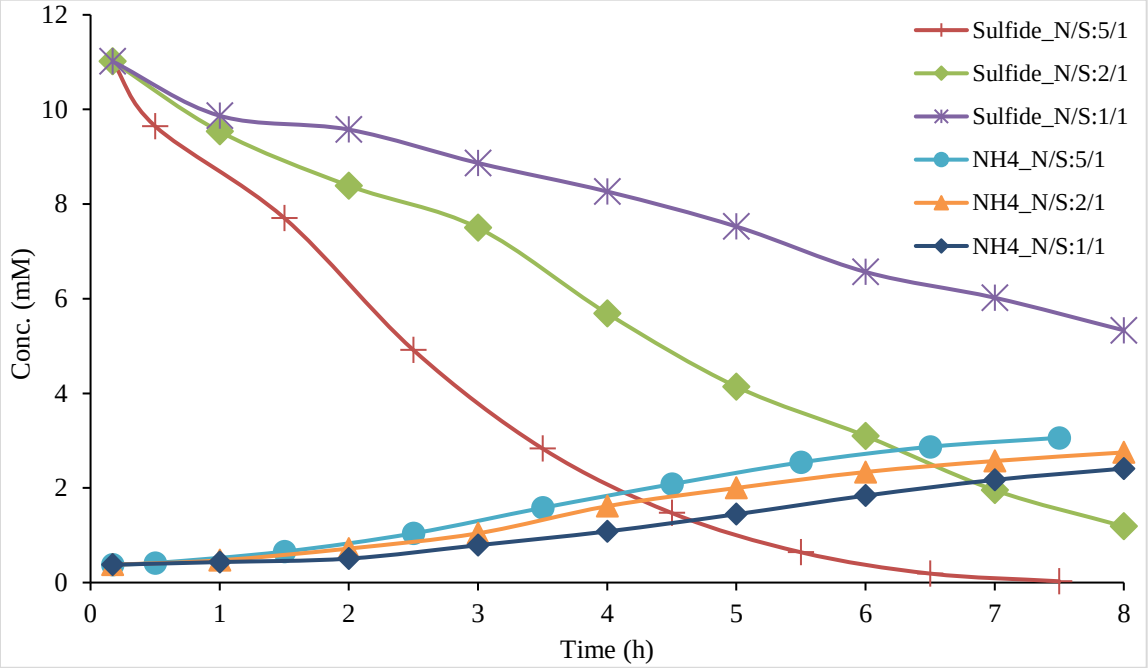


Figure 4.8: Sulfide consumption rate by varying NO_2^- in water at initial pH 6.5

It can be observed from Figure 4.8 that the lower the NO_2^--sulfide concentration ratio, the lower the sulfide consumption rate. Hence, it takes longer time for sulfide disappearance

in the solution with lower NO_2^--sulfide ratio. The result showed that the sulfide-NO_2^- reaction seemed to progress slower at pH 6.5 (Figure 4.8) than at pH 7.2 (Figure 4.7). This can be attributed to the equilibrium shift and speciation of $H_2S/HS^-/S^{2-}$ due to the reduced pH. The NH_4^+ concentrations increased smoothly with time and relative to the initial NO_2^- concentrations. Increase of NH_4^+ raises the pH of the solution to > 9.5. The sulfide-NO_2^- reaction is not favourable at a pH above 10, hence, the rate of reaction decreases and hinders the complete disappearance of sulfide [7].

4.3.5 Thermodynamic Analysis

An equilibrium simulation was done using the HSC Chemistry software to determine the equilibrium constant K and ΔG for equation 4. The reaction between HS^- and Fe^{2+} would reach equilibrium at some point based on the reaction equilibrium criterion [31]. The K value for the reaction ranges from 0.10 to 1.10 at 20–100ºC respectively. The K value indicates that a chemically significant amount of HS^-, Fe^{2+}, and FeS will be present in an equilibrium mixture and the reaction will be reversible. The equilibrium calculation is consistent with the experimental result, as shown in Figure 4.4. The equilibrium simulation of a system containing HS^-, Fe^{2+}, and NO_2^- predicted similar outcomes as the laboratory experiment, however, from the thermodynamic point of view.

4.3.5.1 Modeling Case 1: Simulation of Soured PW System with NO_2^-

Following equations 1 and 4, the input NO_2^- concentration was varied to predict the behavior of other chemical species in the system at equilibrium. FeS, $HS-(S)_2-S^-$, and

NH_4^+ were generated based on the variation of the input NO_2^- concentration. As the input NO_2^- concentration increased from 0 to 20 mM, the following trends were observed; sulfide equilibrium concentration dropped rapidly until it reached a constant at 7 mM input NO_2^- and slowly declined to 0 as input NO_2^- increased to 14 mM, FeS was formed and maintained constant equilibrium concentration over the range of input NO_2^- concentrations, NH_4^+ equilibrium concentration increased and reached a maximum at 6 mM input NO_2^-, then declined to 0 at 13 mM input NO_2^-. Above 13 mM input NO_2^-, the equilibrium NO_2^- concentration started to increase, equilibrium HS^- and polysulfide concentrations increased and reached a maximum at 6 mM input NO_2^-, then remained constant as input NO_2^- concentration increased, the disappearance of NH_4^+ and appearance of equilibrium NO_2^- concentrations at 13 mM input NO_2^-confirmed that NO_2^- was reduced to NH_4^+ as it reacted with sulfide and only a small portion of the NO_2^- was required in the reaction.

4.3.5.2 Modeling Case 2: Simulation of Soured PW System without NO_2^-

This section presents the thermodynamic modeling of a chemical system containing FeS and $FeO(OH)$, as the corrosion products, in soured produced water. Other species included are SO_4^{2-}, HCO_3^-, NH_4^+, CH_3COOH, Fe^{2+}, Na^+, and Cl^- and compositions were based on the measured components in PW (See Table 3.2). The effects of temperature (25-95°C) and pressure (0.1-3 MPa) on the chemistry in the PW system were simulated as shown in Figures 4.9 and 4.10 respectively.

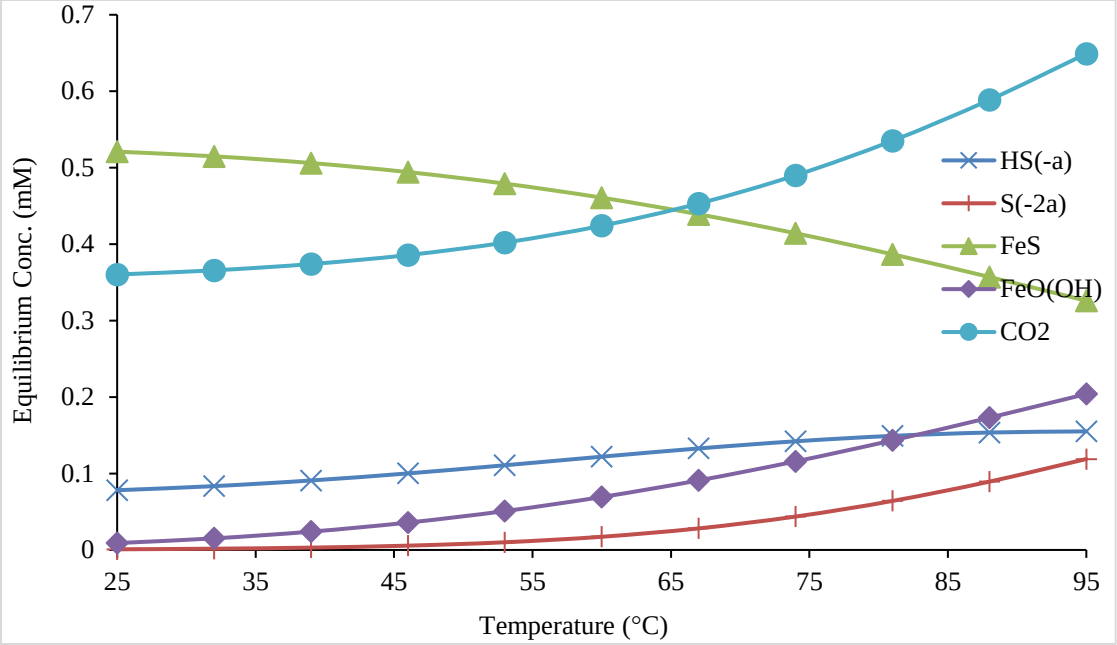


Figure 4.9: Temperature effect on soured PW system at 1 MPa

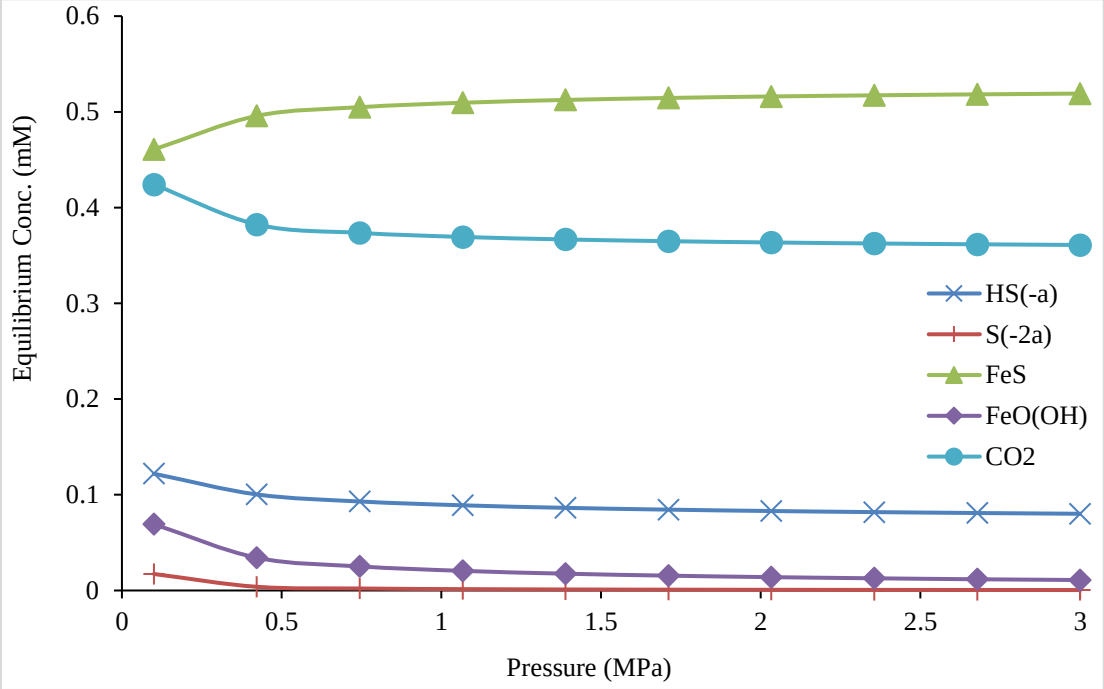


Figure 4.10: Pressure effect on soured PW system at 60°C

From Figure 4.9, FeS, $FeO(OH)$ and S^{2-} are inversely related as the temperature increases. As FeS declines, $FeO(OH)$ and S^{2-} increase smoothly over the temperature range. CO_2 increases with increase in temperature and can impact the pH of the system. By implication, there is a potential drop in the system pH at a higher temperature. Hence, temperature changes can have a high impact on chemical behavior in the PW system. Conversely, Figure 4.10 shows that increase in pressure has little effect on chemical species, especially at high pressures. $FeO(OH)$, CO_2 HS^- and S^{2-} drop sharply while FeS increased from 0.1-0.4 MPa. As the pressure further increases, there are almost no changes in the compositions.

MIC-related microbial groups such as sulfur-oxidizing bacteria (SOB) and methanogens obtain carbon from CO_2 [22]. The FeS layer provides a cathodically reactive surface area, which may accelerate Fe^0 dissolution due to its conductivity [13]. The $FeO(OH)$ deposit can increase the failure risk of the metal resulting in localized corrosion under the FeO(OH) [32].

The model developed in this work could be used as a tool in determining the relative impact of chemical reaction compared to microbial activity on corrosion. Conducting a series of bioreactor corrosion experiments, where the fluid is spiked with various MIC related microbes, and then comparing the results with the model developed here under the same conditions would allow one to evaluate the ineraction on relative impact.

4.4 Summary and conclusions

The chemical environment is an important factor for consideration in MIC propagation. The reaction between sulfide and NO_2^- is one of the key pathways in the nitrate treatment mechanism through which souring is mitigated and MIC controlled. In this work, the chemical transformation of sulfide via NO_2^- reaction in PW was explained using the laboratory experiment. It was observed that the presence of Fe^{2+} in PW interferes with the direct NO_2^- reaction with sulfide. This phenomenon complicates the understanding of sulfide/ NO_2^- reaction kinetics in PW. The sulfide consumption by NO_2^- in seawater has shown the consumption of sulfide obeys pseudo-first-order kinetics and leads to the production of elemental S^0 via polysulfide and ammonium under the experimental conditions. Since no published reaction rate describes sulfide/ NO_2^- reaction in PW or seawater system, the reaction data can fill the information gaps that are critical for understanding the chemical pathway of nitrate treatment mechanism outside the microbial inhibitions of sulfide formation. The study of the sulfide/ NO_2^- reaction in the water at an initial pH 7.2 indicated the tendency of the reaction proceeding without the potential impact of buffer. The rate of sulfide/ NO_2^- reaction obtained in water and seawater were consistent under the experimental conditions studied.

It is recommended for future studies to investigate the effect of pH (e.g. pH 5-7) and elevated temperatures (e.g. >45°C) on the sulfide/NO_2^- chemical transformation in seawater and PW systems. Most sulfide and NO_2^- reactions are pH and temperature-dependent and can make a great difference in the system chemistry. An in-depth study on the rate of

sulfide disappearance via NO_2^- in the PW system could be achieved by using more sophisticated and well-designed experiments to decouple the competing reactions and generate a reliable kinetic data. Corrosion experiments in a bioreactor with similar compositional matrix and conditions as well as microbial community analysis can be matched with the model and experimental outcomes of the current study. The comparison would lead to better understanding of the microbial-chemcal interaction behavior and potential impact on MIC.

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5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Overall Conclusions

The investigation approaches and understanding of MIC are evolving across multiple disciplines. This thesis has made a significant step toward describing the chemical environment impacting MIC in the offshore platform, an aspect that has received less attention from researchers in the past. The research work provided an insight for the understanding of MIC chemistry, a strong basis for further studies and data for the development of an integrated MIC model which may include MIC mechanism, predictive, and management tools for offshore oil and gas industries. The following are the highlights of the overall thesis outcomes.

- Reviewed and presented a detailed description of various groups of microorganisms associated with MIC (nutrients, Physico-chemical conditions, and metabolic products), the chemical environment in the oil and gas operations (produced water systems, separators, and flowlines), and corrosion chemical products found in different corrosive environments.
- Identified key chemical species in various environments followed by an explanation of the chemical species utilization and production relationships impacting MIC.
- Described the chemical-microbial interactions; the linkages between the chemical environment, environmental factors, and electrochemical processes with respect to microbial activities causing MIC.

- Conducted thermodynamic analysis of the identified chemical species to determine stability and informed the chemical environment modeling.
- Equilibrium modeling of the chemical environment predicted the S and N transformation behavior as a function of temperature, pressure, and compositions, similitude to the offshore oil and gas topside facilities. The simulation presented an approach to monitor the chemistry of PW systems which in turn will enhance the understanding of MIC propagation and mitigation.
- Kinetic modeling of the sour-oxic environment in seawater showed a similar trend with the wet-lab experiment in PW. An indication that the kinetic data for sulfide oxidation in seawater can be adopted for PW systems under similar conditions.
- Experimental investigation of S and N transformation in water, seawater, and PW provided a better understanding of the sulfide-nitrite reaction kinetics and dynamic conditions affecting it. The reaction was impacted by Fe^{2+} in PW to form insoluble FeS and the reaction may not proceed at above pH 10.

5.1.1 Review and analysis of MIC: the chemical environment

Many studies on MIC focused on targeted microorganisms, and microbial activities causing MIC in isolation of the surrounding environment chemistry where it occurs. The chemical environment is an important factor to be considered in MIC propagation. It is the source and sink of microbial nutrients and bye-products respectively and provides a suitable medium for the transformation of the chemical species impacting microbial activities. This section of the thesis presented pertinent information on MIC and the

surrounding fluid chemistry in the oil and gas topside systems through a detailed review and analysis. This approach systematically examined how various contributors and their interactions impact MIC propagation. The major chemical species/compounds that contribute to MIC in oil and gas operations were identified. These include various microorganisms associated with MIC (nutrients, metabolites, and growth conditions), surrounding chemical environment, and chemical compounds resulting from different corrosive environments. Critical arguments and illustrations were presented about microbial-chemical interactions in MIC processes. The study identified the areas of diffuse understanding and information gaps such as the rate at which chemical species are consumed, generated, and/or transformed from one form to the other through microbial actions and/or chemical means. The information is vital in developing a robust MIC mechanism and risk models and allows a better deployment of corrosion management strategies.

5.1.2 Equilibrium and kinetic modeling

Microbially mediated reactions associated with MIC have been studied extensively, without considering the relative impact of the chemically driven transformations of reactive species due to the changing operating parameters (temperature, pressure, pH, and composition). This section of the thesis demonstrated the dynamic behavior of the chemical environment as a function of temperature, pressure, and composition to represent the offshore oil and gas topside conditions. Equilibrium and kinetic models were used to simulate the chemistry of fluids to understand the transformation of various chemical

species and the potential impact on MIC in a given environment. The sour-oxic-nitrite environment was considered in this work. The outcomes of the modeling study were the chemical species composition and the prediction of FeS, $FeO(OH)$, and Fe_2O_3 as the key corrosion products and S^0 as a function of operating parameters in a sour-oxic-nitrite environment. A low concentration of NO_2^- favored the formation of S^0 instead of SO_4^{2-} with sufficiently high NO_2^-. These compounds agree with the chemical transformation pathways described in the literature. The staged thermodynamic simulation and kinetic modeling approach demonstrated in this work can serve as tools to better understand the chemistry of S and N species in the offshore oil and gas topside separation process and an indication of the contributory effect of the chemical transformation on the overall corrosion. The study will inform further investigation on the chemical environment impacting MIC (e.g. modeling of other kinds of the chemical environment; sour–CO_2–nitrite) and the development of an integrated chemical, microbial and risk model for a better deployment of corrosion management strategies in the offshore oil and gas topside separation processes.

5.1.3 Experimental investigation of sulfide–nitrite chemical transformation

Little is known about the reactivity between S and N species and potential impacts on corrosion. It is believed that sulfide can react chemically with nitrite in the PW system, however, there are no kinetic studies conducted on the sulfide-nitrite chemical reaction in produced fluids targeting the offshore oil and gas applications. This section of the thesis presented a reactivity study of sulfide and nitrite in different media including PW, seawater,

and water. Experiments suggested that sulfide in these media could be oxidized by nitrite to polysulfide, elemental S^0, and NH_4^+ under slightly acidic to slightly basic conditions. The kinetic data were generated under the experimental conditions (45ºC, 1 atm, and pH: 6.5-7.5). According to the S and N biotic transformation study conducted by the microbiology group at the University of Calgary, it is difficult to attribute the nitrite losses in the experimental replicates solely to biotic or abiotic reactions, quantify the relative contribution, and measure the rate of the chemical reaction. Our experimental study fills the gap of the vital information that might be missing in the short term due to the reactivity of S and N independent of microbial actions. An experiment in PW, seawater, and water containing sulfide and nitrite showed sulfide to be chemically consumed in under 10 hours when nitrite is present. The outcome of the chemical experiments provided an insight into the rate of sulfide and nitrite consumptions and the impact of the rapid formation of FeS in soured PW. The data could be integrated into the microbial mechanisms to develop a robust MIC model.

5.2 Recommendations

From the chemistry perspective, a deeper understanding of the MIC chemical environment could be achieved by identifying and analyzing more compounds in various chemical environments with major contributions to MIC propagation and/or inhibition, chemical species transformation behavior under a wider range of operating conditions, and chemical-microbial interaction pathways impacting MIC.

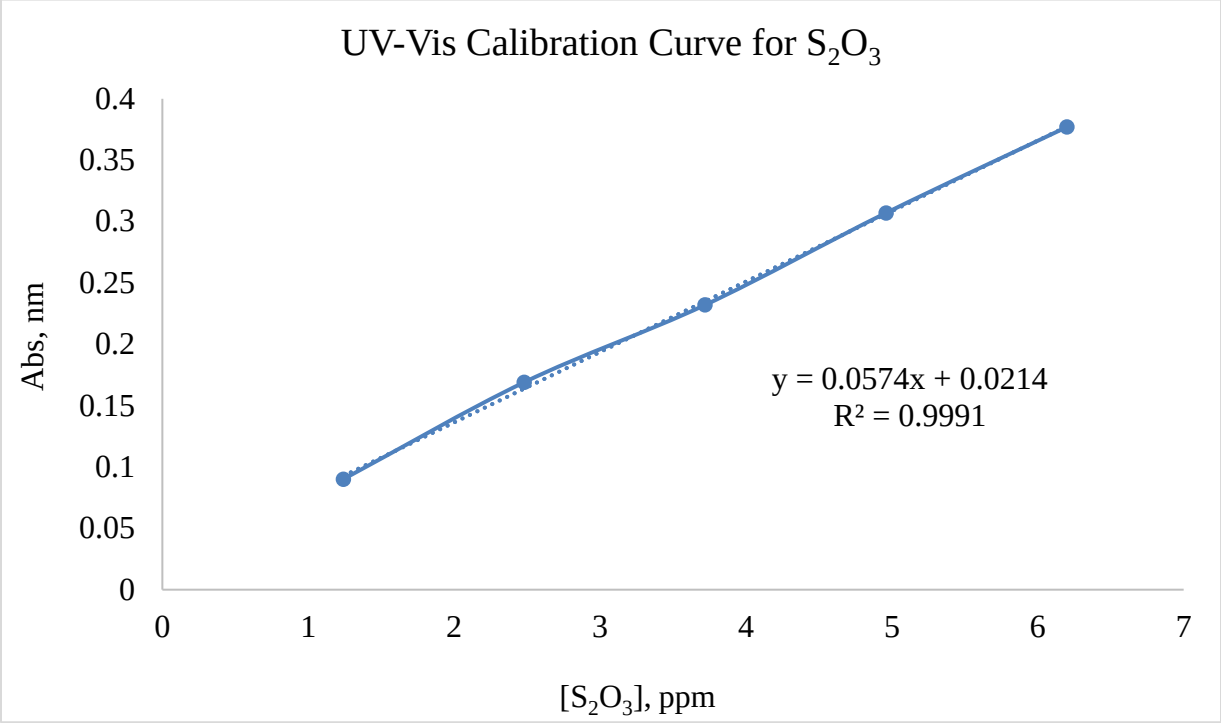
An equilibrium model approach is an essential tool for investigating the thermodynamic behavior of important chemical species in PW systems and the potential corrosion products at different operating conditions. The approach developed in this research could further be applied to other chemical environments (e.g. sulfide-CO_2-nitrite) for better understanding and comparison with various chemical environments. Given that the equilibrium model is based on the thermodynamic principles of infinite time for reaction, further research should place more emphasis on the kinetic approach to simulate chemical environments from available data. This will allow for a better understanding of the rate of chemical species transformation and the compositional dynamics of the system.

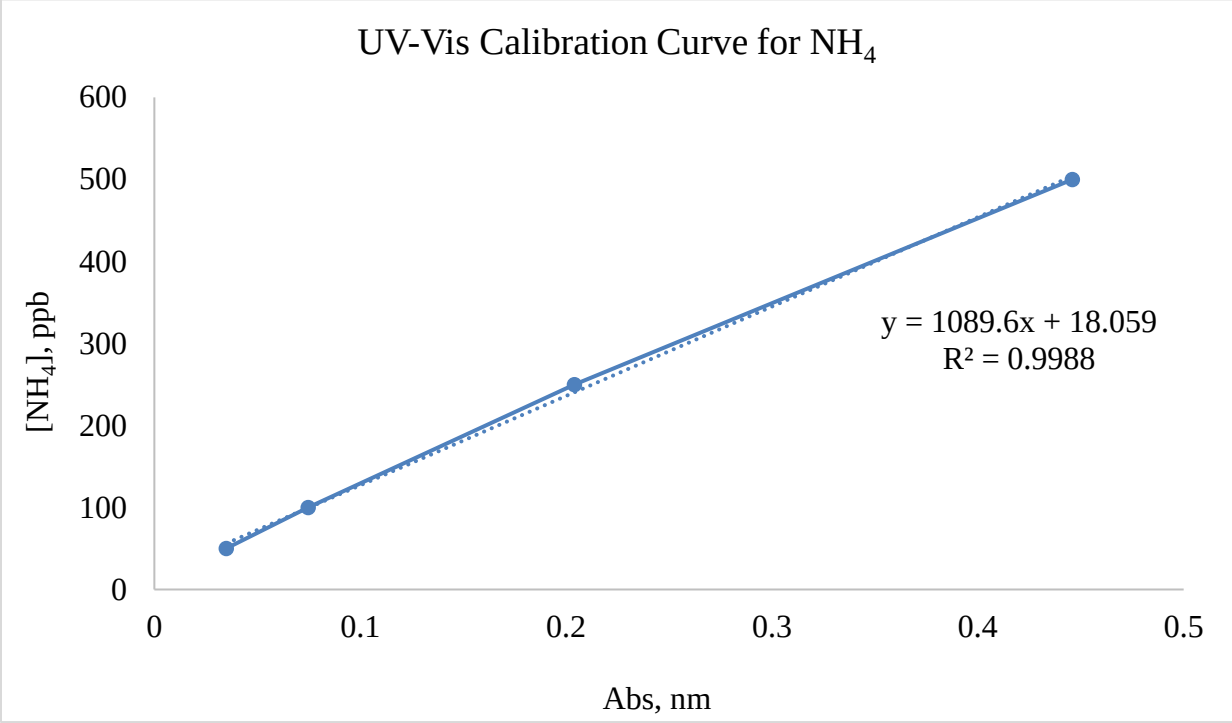
While taking the advantage of the information presented in this work, an in-depth study is encouraged to consider the development of an integrated chemical, microbial, and risk model for a better deployment of corrosion management strategies in the offshore oil and gas topside separation process. This can be achieved by coupling the chemical kinetics with the microbial models (e.g. Michaelis–Menten and Monod kinetics) to predict the consumption and production rates of important chemical species impacting MIC. The rate data will account for the combined effect of chemically driven and microbially mediated reactions, which can be incorporated into MIC risk models for more realistic predictions.

Also, experimental studies are valuable in investigating the reactivity of key chemical reactions, filling data gaps, and validating the models. Identifying more important chemical reactions related to other chemical environments would be a starting point for further investigation. It is recommended for future studies on the sulfide/NO_2^- chemical

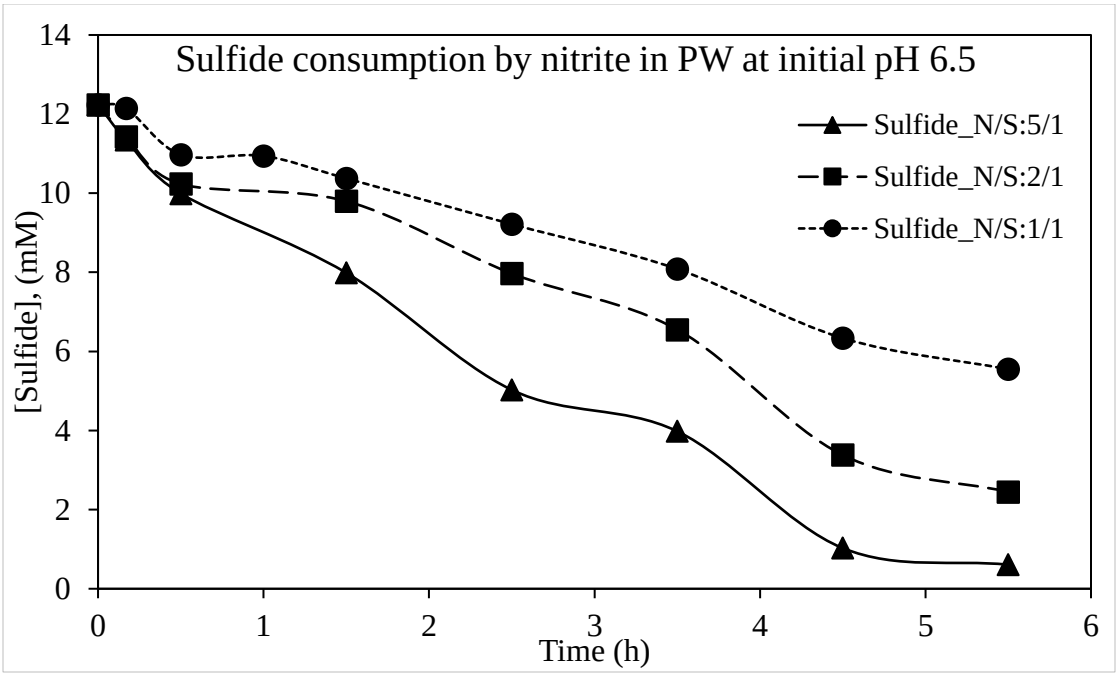
transformation in seawater and PW systems to investigate the effect of pH (e.g. pH: 4–10, buffered and unbuffered), varying initial concentrations, and elevated temperatures under controlled laboratory conditions. Most sulfide and NO_2^- reactions are pH and temperature-dependent and can make a great difference in the system chemistry. A better understanding of the rate of sulfide and NO_2^- disappearance in the PW system could be achieved by using a more sophisticated analytical method and well-designed experiments to decouple competing reactions and generate reliable kinetic data. More reactions involving polysulfides, thiosulfate, and polythionates should be investigated and analyzed for potential impacts on MIC.

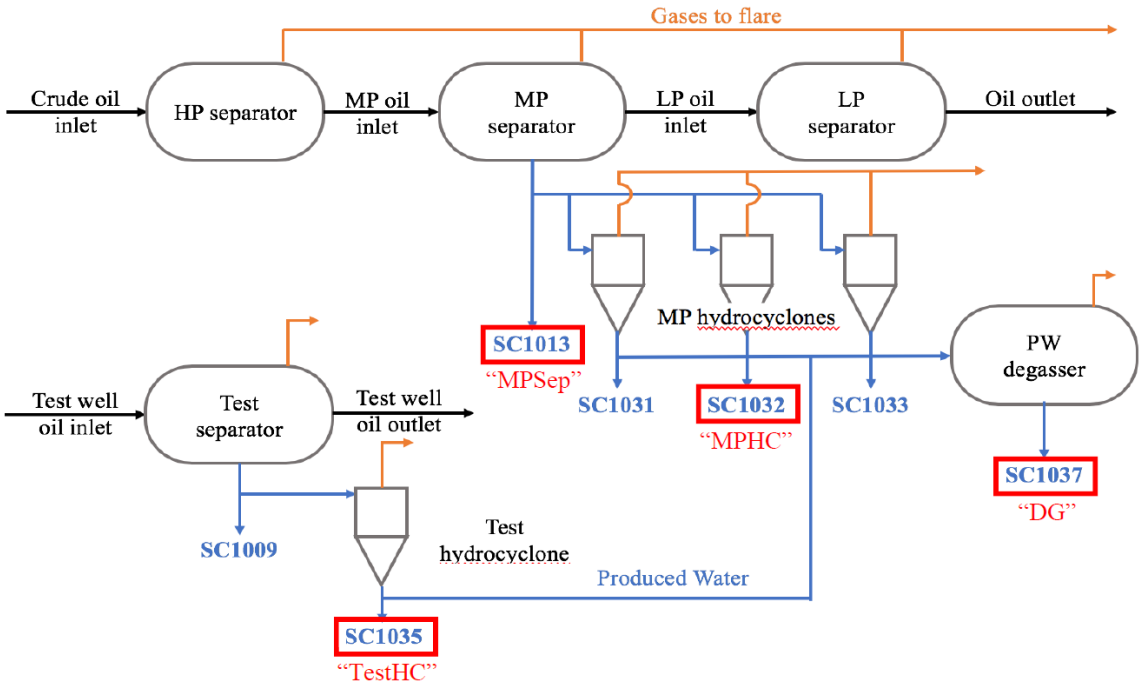
Appendix


UV-Vis Calibration Curve for S_2O_3
Abs, nm
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
1
2
3
4
5
6
7
y = 0.0574x + 0.0214
R² = 0.9991
[S_2O_3], ppm

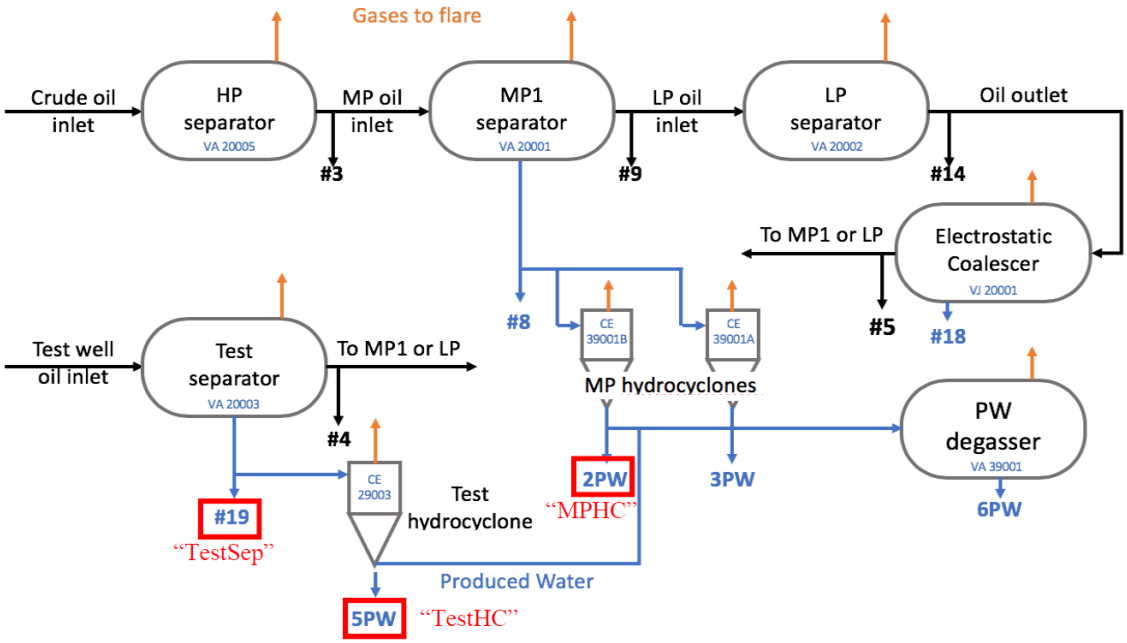

UV-Vis Calibration Curve for NH_4
[NH_4], ppb
600
500
400
300
200
100
0
0
0.1
0.2
0.3
0.4
0.5
y = 1089.6x + 18.059
R² = 0.9988
Abs, nm

Wet lab Experimental Set up

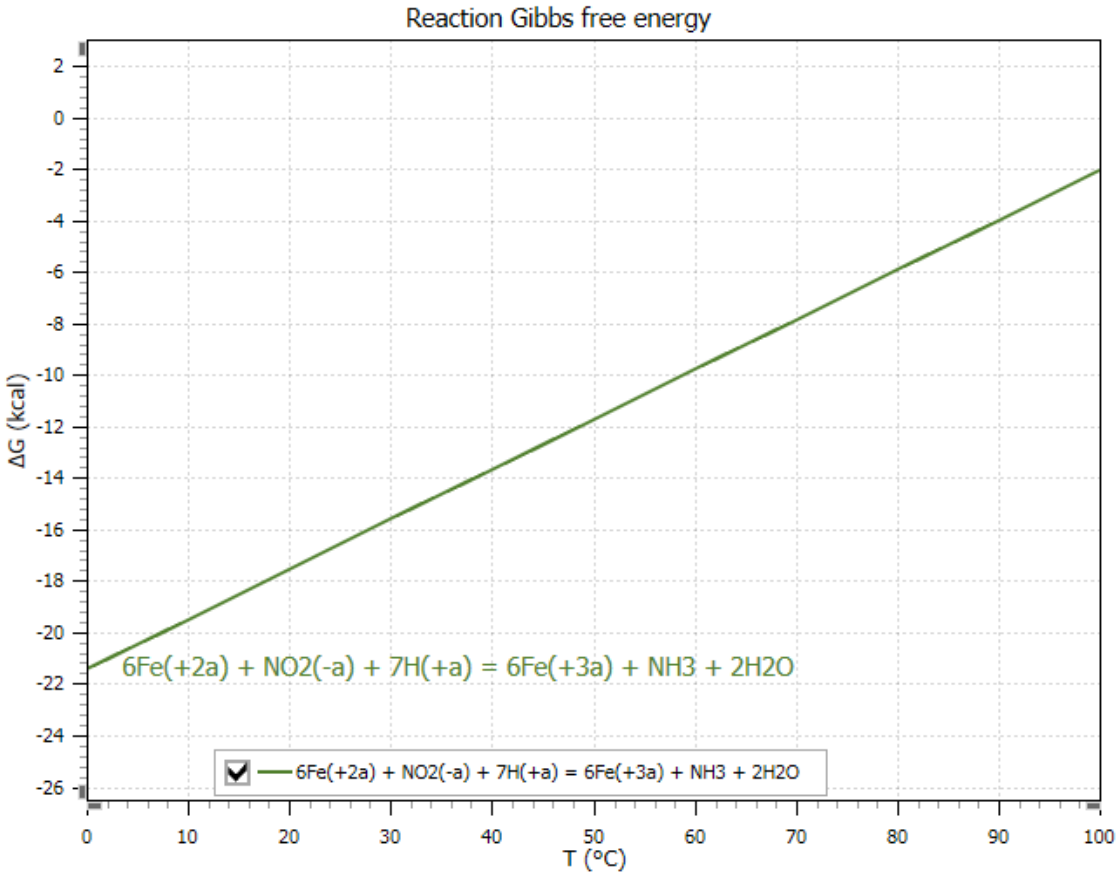


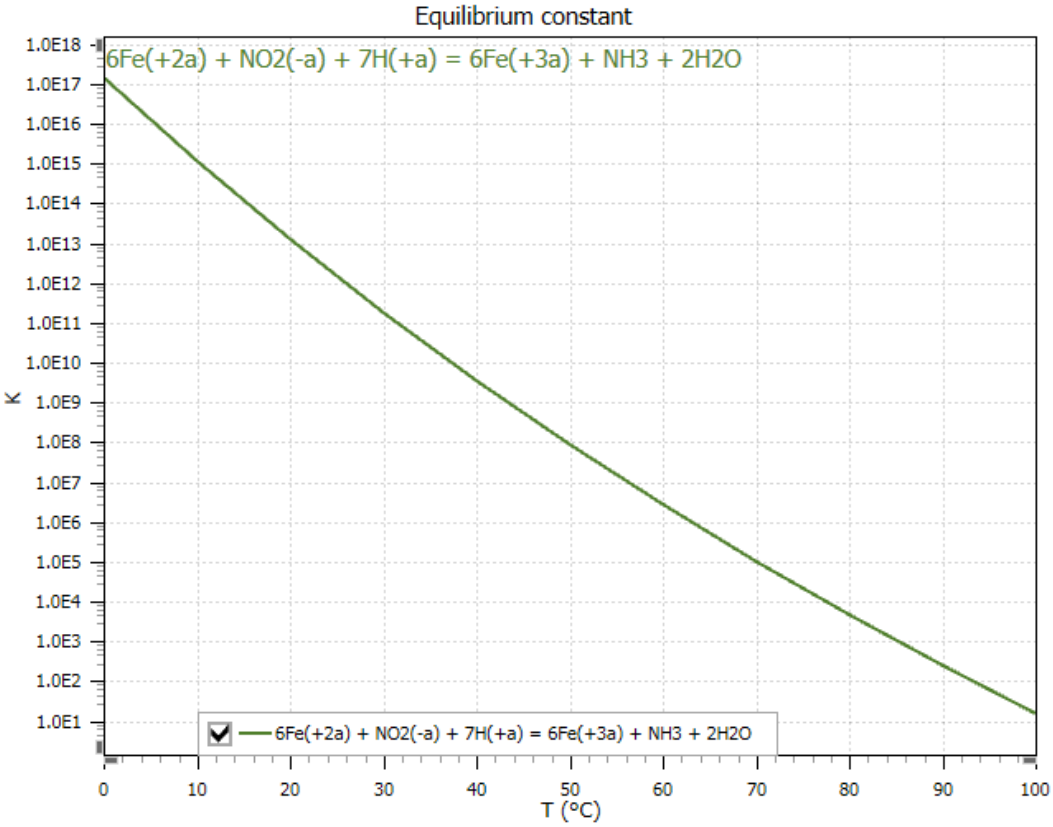


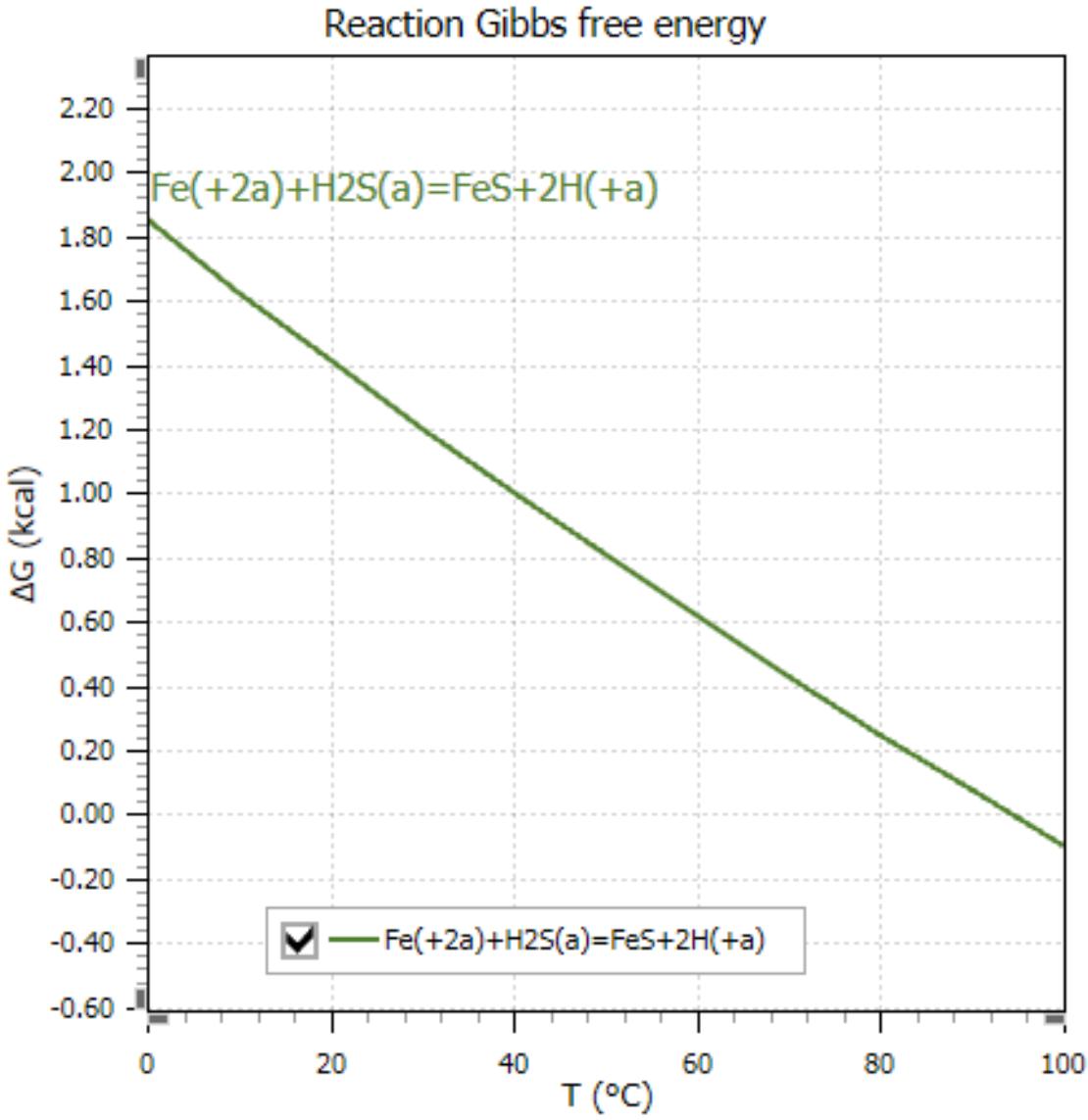
Schematic Diagram for Ofshore Oil and Gas Platform 1 Produced Water Sampling Points

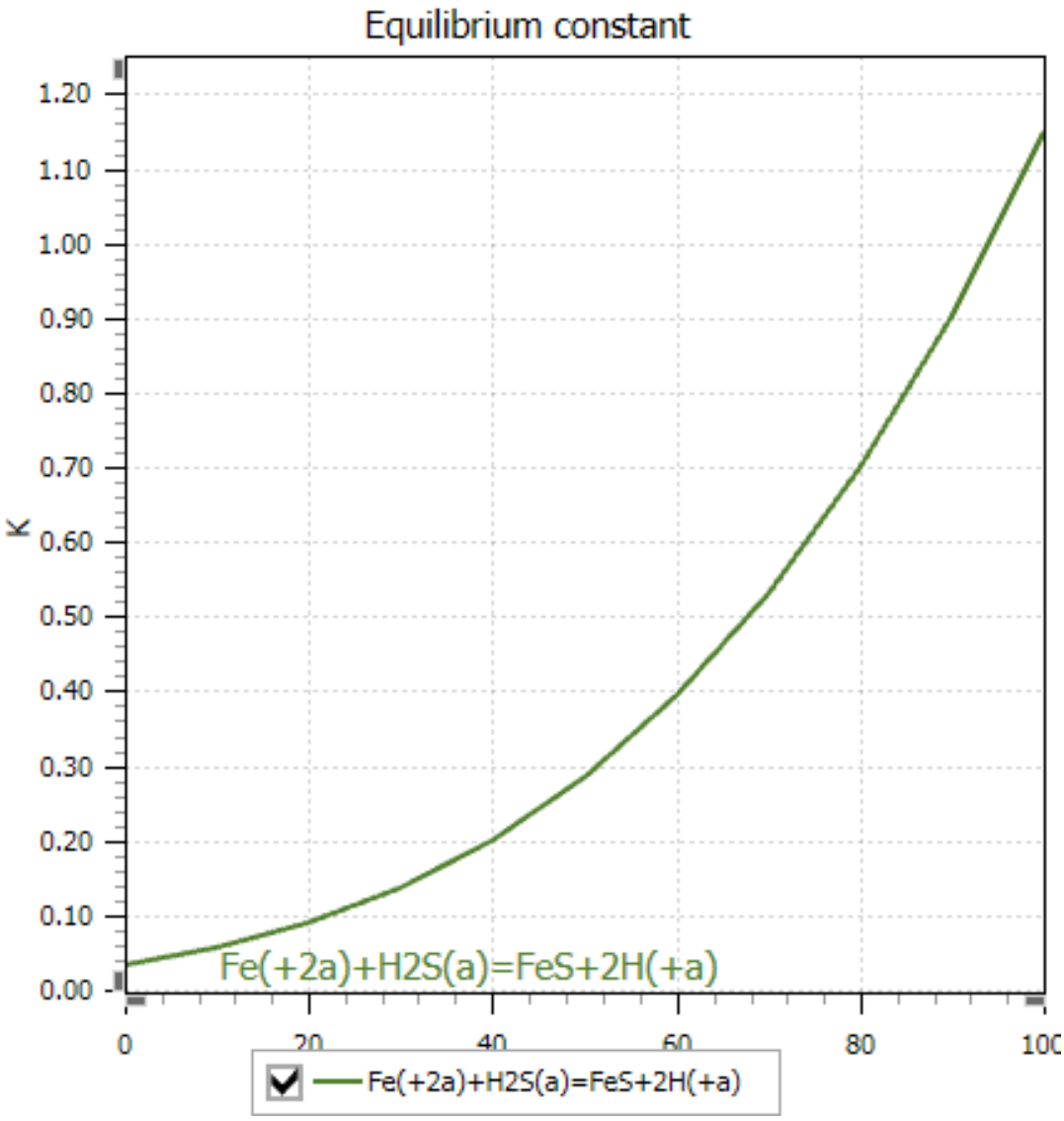


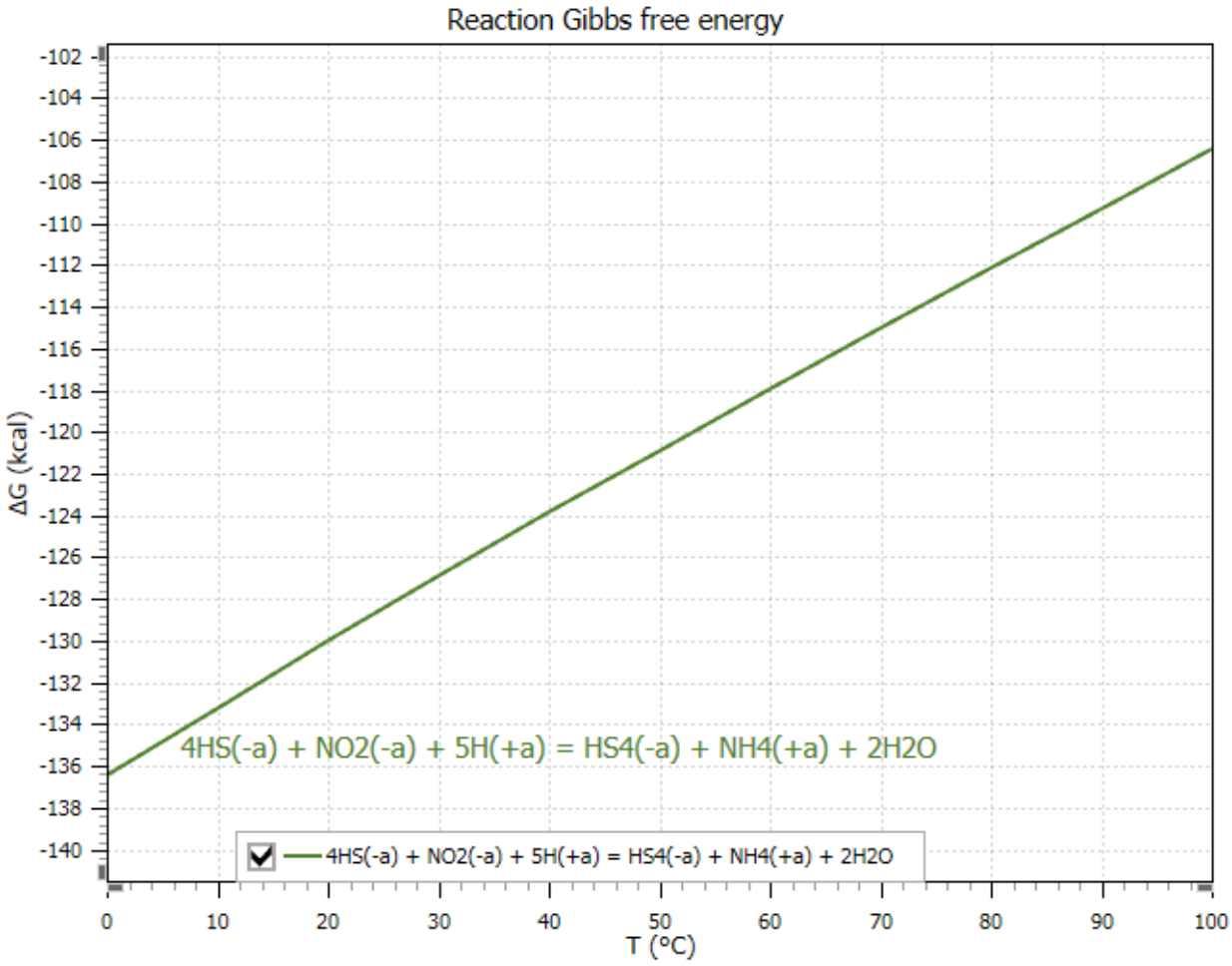
Schematic Diagram for Ofshore Oil and Gas Platform 2 Produced Water Sampling Points

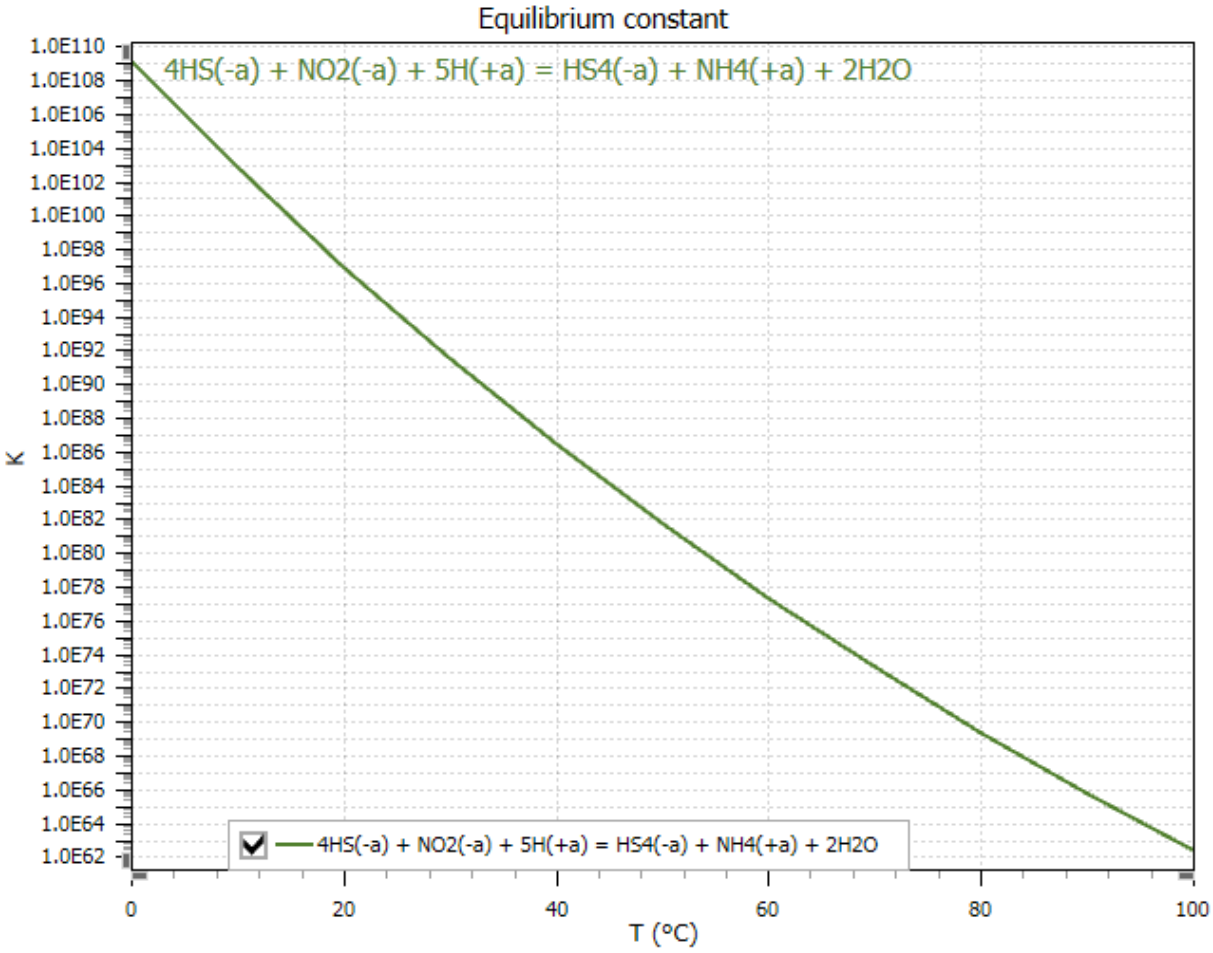

Reaction Gibbs free energy
ΔG (kcal)
T (°C)
6Fe(+2a) + NO2(-a) + 7H(+a) = 6Fe(+3a) + NH3 + 2H2O
6Fe(+2a) + NO2(-a) + 7H(+a) = 6Fe(+3a) + NH3 + 2H2O

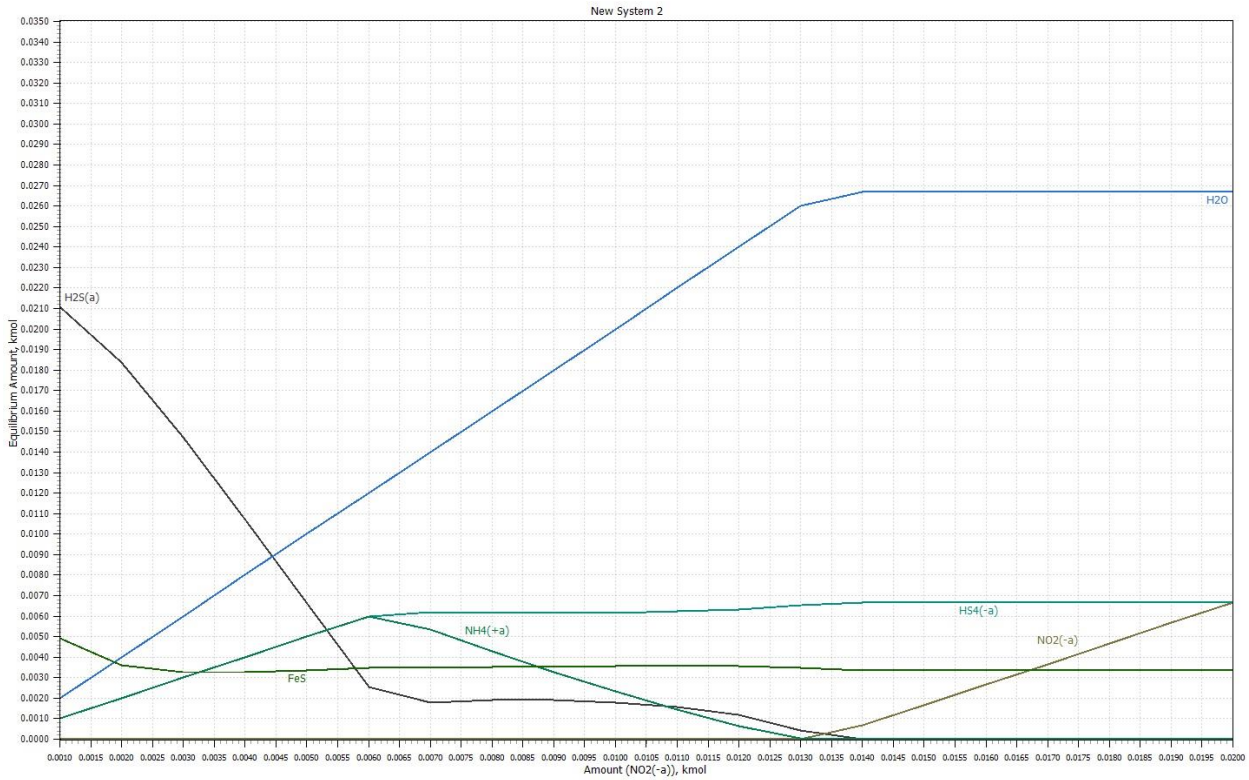

Equilibrium constant
6Fe(+2a) + NO2(-a) + 7H(+a) = 6Fe(+3a) + NH3 + 2H2O
K
1.0E18
1.0E17
1.0E16
1.0E15
1.0E14
1.0E13
1.0E12
1.0E11
1.0E10
1.0E9
1.0E8
1.0E7
1.0E6
1.0E5
1.0E4
1.0E3
1.0E2
1.0E1
0
10
20
30
40
50
60
70
80
90
100
T (°C)
6Fe(+2a) + NO2(-a) + 7H(+a) = 6Fe(+3a) + NH3 + 2H2O

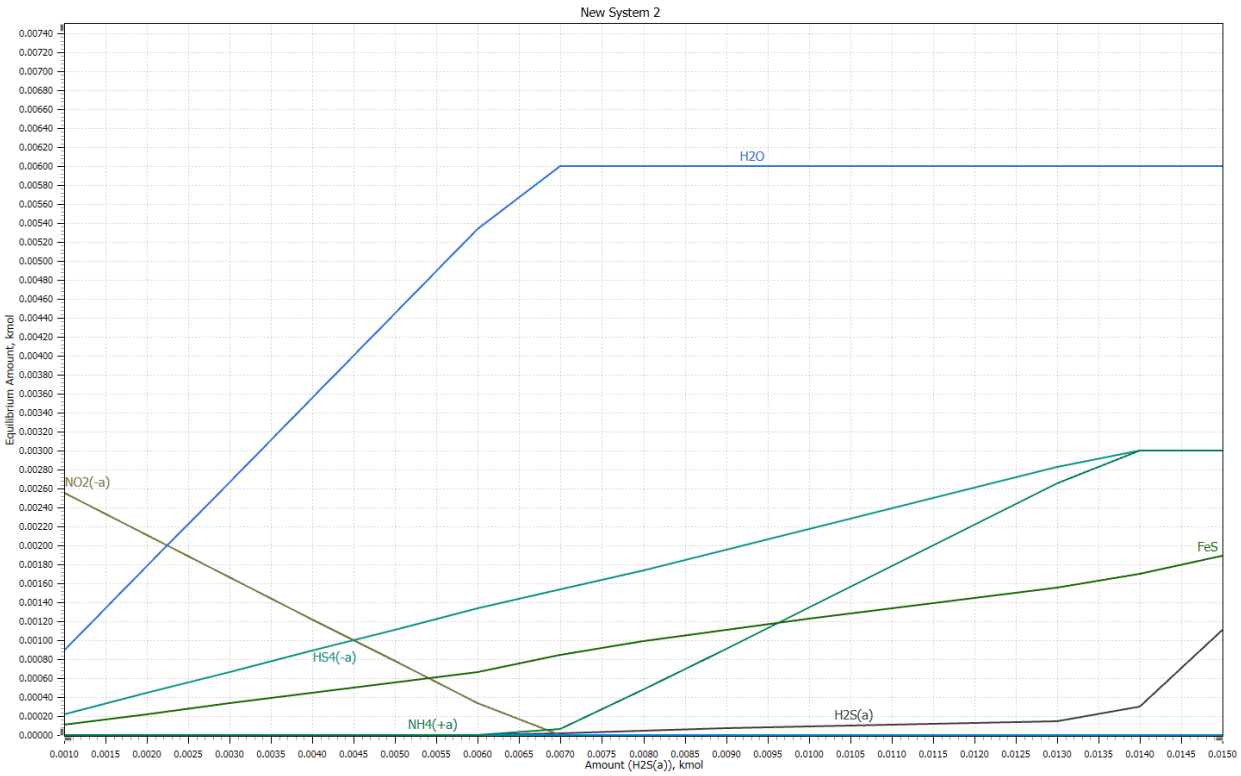

Reaction Gibbs free energy
Fe(+2a)+H2S(a)=FeS+2H(+a)
ΔG (kcal)
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
-0.60
0
20
40
60
80
100
T (°C)
Fe(+2a)+H2S(a)=FeS+2H(+a)


Equilibrium constant
K
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
20
40
60
80
100
Fe(+2a)+H2S(a)=FeS+2H(+a)
Fe(+2a)+H2S(a)=FeS+2H(+a)


Reaction Gibbs free energy
ΔG (kcal)
T (°C)
4HS(-a) + NO2(-a) + 5H(+a) = HS4(-a) + NH4(+a) + 2H2O
4HS(-a) + NO2(-a) + 5H(+a) = HS4(-a) + NH4(+a) + 2H2O


Equilibrium constant
4HS(-a) + NO2(-a) + 5H(+a) = HS4(-a) + NH4(+a) + 2H2O
K
1.0E110
1.0E108
1.0E106
1.0E104
1.0E102
1.0E100
1.0E98
1.0E96
1.0E94
1.0E92
1.0E90
1.0E88
1.0E86
1.0E84
1.0E82
1.0E80
1.0E78
1.0E76
1.0E74
1.0E72
1.0E70
1.0E68
1.0E66
1.0E64
1.0E62
0
20
40
60
80
100
T (°C)
4HS(-a) + NO2(-a) + 5H(+a) = HS4(-a) + NH4(+a) + 2H2O


New System 2
Equilibrium Amount, kmol
Amount (NO2(-a)), kmol
H2O
H2S(a)
HS4(-a)
NH4(+a)
NO2(-a)
FeS


New System 2
Equilibrium Amount, kmol
Amount (H2S(a)), kmol
H2O
NO2(-a)
HS4(-a)
NH4(+a)
H2S(a)
FeS